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Influence of irradiation with fast electron beam on energy transport in praseodymium-ion doped phosphates

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ABSTRACT

This paper reports the spectroscopic properties of praseodymium-doped phosphates, $KLuP_2O_7$, $Sr_9Sc(PO_4)_7$, K_3Lu (PO_4)₂ doped with Pr^{3+} ions. Spectra of photoluminescence (PL) upon selective UV photon excitation, PL excitation spectra as well as luminescence spectra and decay kinetics upon pulse synchrotron X-ray excitation were studied. Recordings of luminescence spectra were done with pure samples and after irradiating with fast electrons (E = 10 MeV) using linear electron accelerator. The absorbed dose varied in the range of 150–300 kGy. Pure samples demonstrated three typical channels of emission: interconfigurational d - f transitions, intraconfigurational f - f transitions and defect-related luminescence. After irradiating, two scenarios of changing optical properties were investigated: increasing of defect-related luminescence impact in total light output and "suppressing" of defect-located energy emission.

1. Introduction

Investigation of new scintillating materials pays a lot of attention to rare earth-doped inorganic compound due to potential variety of their applications in different spheres, such as detecting systems, medical tomography, nuclear physics, etc. Most properties of rare-earth ions emission are determined by intra- and interconfigurational transitions. Emission transitions 5d - 4f of Pr^{3+} appear when strong enough crystal field moves the lowest $4f^{1}5d^{1}$ excited state lower than ${}^{1}S_{0}$ state [1]. Three types of emission are observed in inorganic scintillators doped with Pr^{3+} ions: interconfigurational d - f transitions located in the UV range (250–320 nm), intraconfigurational f - f transitions (lines in the visible spectral range) and defect-related luminescence [2,3]. Cerium ions are in favour for industry, but praseodymium has shorter decay time, and its d - f emission is located at shorter wavelengths. In comparison with impurity Ce³⁺ ions, praseodymium emission is in higher energy region and has shorter lifetime (20-30 ns instead of 30-60) [4-9]. Praseodymium is actual object for new materials investigating, series of measurements have been performed featuring synchrotron radiation [1,2] and different materials groups studying [10,11]. Results of non-irradiated spectroscopy measurements of studied samples were previously published in Refs. [10,12–17].

Optical and electrophysical properties modifying with fluxes of highlevel particles is not so common research object due to the theory of electrons, e.g., influence on solids. In most cases, such interactions cause only negative effects, such as decreasing light output, significant structural changes, changing of solids types, etc. The authors hope to find a positive effect on the optical properties by subjecting the Pr-doped materials to high radiation fluxes of electrons. Studied samples – phosphates with Pr^{3+} -impurity ions have already been approved as potential convenient scintillators with appropriate emission levels of 250–300 nm fast d-f transitions with average lifetime of 15–20 ns, and Z_{eff} varying in 35 ... 45 range.

2. Materials and methods

Polycrystalline samples of Pr^{3+} -doped KLuP₂O₇, Sr₉Sc(PO₄)₇, K₃Lu (PO₄)₂, LiSrPO₄ were synthesized using a solid state reaction and PXRD verified for phase purity at the Laboratory of Luminescent Materials, University of Verona (Italy).

KLuP₂O₇ (1 mol. % Pr³⁺): Powder microcrystalline material has a stoichiometry of KLu_{0.99}Pr_{0.01}P₂O₇ (*i.e.*, containing 1 mol. % Pr³⁺ substituting for Lu³⁺). The constituent high purity raw materials KNO₃, (NH₄)₂HPO₄, Lu₂O₃, and Pr₆O₁₁ (the last two reagents 4 N) were mixed, and heat treated in a horizontal furnace in air for 1 h at 400 °C and 24 h at 750 °C with intermediate regrinding. The phase purity of the prepared sample was examined using powder X–ray diffraction (PXRD) technique with a Thermo ARL X'TRA powder diffractometer, operating in the

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Fig. 1. (a): XRL spectra of studied phosphates. (b): XRL decay kinetics excited with high frequency X-ray synchrotron radiation, (black and green curves), approximation lines (red and blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Bragg–Brentano geometry and equipped with a Cu anode X–ray source (K_{α} , $\lambda = 1.5418$ Å) with a Peltier Si(Li) cooled solid–state detector. The obtained PXRD pattern was fully compatible with ICDD Card No. 01–076–7386 [12,18]. The crystal structure of KLuP₂O₇ offers only one site for Lu³⁺ (or Pr³⁺) with a coordination number of 6 and point symmetry C_1 .

Sr₉Sc(PO₄)₇ (1 mol. % **Pr**³⁺): The XRD pattern revealed perfect matching with the reference JPCDS data that indicates the presence of a single-phase structure [19].

K₃Lu(PO₄)₂ (1 and 5 mol. % Pr³⁺): K₂CO₃ (99%), (NH₄)₂HPO₄ (>99%), Lu₂O₃ (Aldrich, 99,99%) and Pr₆O₁₁ (Aldrich, 99.999%) powders were mixed and pressed into pellets under a load of 10 tons. The samples underwent two thermal treatments under air atmosphere (600 °C for 4 h and 950 °C for 1 h), with intermediate grindings. At room temperature this host crystallizes with a trigonal unit cell, \overline{P} 3 space group. For this host material two phase transitions are known to occur at lower temperature around 250 and 140 K [9–11]. All the diffraction peaks in the XRD pattern of 1% Pr³⁺ doped K₃Lu(PO₄)₂ [14].

LiSrPO₄ (1 mol.% Pr³⁺): Stoichiometric amounts of SrCO₃ (>98.0%), Li₂CO₃ (>99.0%), (NH₄)₂HPO₄ (>99.0%) and Pr₆O₁₁ (99.999%) were mixed, pressed to a pellet, and introduced in a covered alumina crucible. The pellet was heated at 1300 °C for 3 h in a horizontal furnace under air at atmospheric pressure. The LiSrPO₄ orthophosphate possesses a hexagonal structure with lattice parameters *a* = 5.0040 Å, *c* = 24.6320 Å and P65 space group. The XRD pattern revealed perfect matching with the reference ICDD data that indicates the presence of a single-phase structure [15].

The experimental results presented in this paper were obtained applying different techniques. Photoluminescence (PL) and PL excitation spectra upon excitation in the UV energy range (from 3.5 to 5.8 eV) were measured at the Laboratory of Solid State Physics, Ural Federal University. To excite the luminescence a 400 W deuterium lamp and a LOMO DMR-4 primary prismatic double monochromator were used. A secondary DMR-4 monochromator equipped with a Hamamatsu R6358-10 photomultiplier tube (PMT) was used to detect the emission signal. A BSV-2 X-ray tube (30 kV, 10 mA, Cu anode) was used for X-ray excited luminescence (XRL). XRL was detected using a LOMO MDR-23 monochromator and a FEU-106 PMT.

The measurements of decay kinetics and emission spectra upon excitation with non-monochromatic X-ray synchrotron radiation (E = 3-60 keV, pulse FWHM ~ 1 ns, frequency ~ 8 MHz) were performed at room temperature at the beamline #6 of the VEPP-3 storage ring at Budker Institute of Nuclear Physics (Russia). Stroboscopic method of electron-optical chronography with sub-nanosecond time resolution was used. The detection system included a SOL Instruments MS2004 monochromator equipped with a high-speed LI-602 dissector [10].

All emission spectra were corrected for the spectral sensitivity of the detection systems. PL excitation spectra were corrected for wavelength dependent photon flux variation using yellow lumogen.

3. Results and discussion

3.1. Pulsed X-ray excited spectroscopy

X-ray excited luminescence spectroscopy results are presented in Fig. 1 (a). The spectrum of KLuP₂O₇ is dominated by emission bands corresponding to $4f^{1}5d^{1} - 4f^{2}$ interconfigurational radiative transitions in Pr³⁺ ion. In the region of 380–560 nm (2.21–3.26 eV) wide weak bands of defect-related luminescence are observed. Weak emission lines corresponding to intraconfigurational $4f^{2} - 4f^{2}$ transitions are located near 490 and 612 nm.

According to the features of XRL spectra, the presence of energy transfer from the host to both Pr^{3+} impurity centers and defects can be observed. This fact should obviously limit the quantum yield for recombinational luminescence of Pr^{3+} impurity centers due to formation of competing path for capture of charge carriers. According to XRD analysis, XRL spectrum of 1% Pr^{3+} K₃Lu(PO₄)₂ corresponds to the trigonal phase and XRL spectrum of 5% Pr^{3+} K₃Lu(PO₄)₂ corresponds to the monoclinic phase of the investigated crystal. This means that increasing the concentration of Pr^{3+} ions shifts the phase transition from monoclinic to trigonal phases to a temperature higher than 295 K. The

yield of $4f^2 - 4f^2$ transitions in Sr₉Sc(PO₄)₇ is about 9 times more than $4f^15d^1 - 4f^2$ output.

The value of d-f/f-f ratio is as bigger as the Stokes shift is lower. The domination of interconfigurational transitions is possible only with Stokes shift smaller than 3200 cm⁻¹ [1]. The contribution of defect-related luminescence in Sr₉Sc(PO₄)₇ emission spectrum is rather high, what indicates a significant role of this charge carriers capture channel in light output, decreasing the yield of inter- and intraconfigurational transitions. LiSrPO₄ emission spectrum contains a set of bands for two transition types $4f^15d^1 - 4f^2$ at 240 and 267 nm and $4f^2 - 4f^2$ in 580–650 nm region. d - f/f - f ratio here is rather high (about 3.25) but potassium compounds are better in this respect – they present 14.28 and 9.1 for K₃Lu(PO₄)₂ with 1% and 5% praseodymium impurity and 12.5 for KLuP₂O₇.

The relative ratio of d - f/f - f transitions yield depends on excitation energy and measurement temperature. At room temperature d - f/f - fratio is lower with band-to-band excitation than at inner-center excitation. According to Srivastava et al. [1], to produce the domination of $4f^{1}5d^{1} - 4f^{2}$ emission over intraconfigurational $4f^{2} - 4f^{2}$ transitions, the compound has to demonstrate small Stokes shift. In Pr³⁺ ion this threshold amounts 3200 cm⁻¹, or 0.4 eV. If both types of emission lines can be observed in studied sample, it can be concluded then, that the reason of their presence is big Stokes shift.

For better understanding it must be underlined that luminescence decay kinetics curves in most cases are well fitted with multiexponential approximation (1):

$$\mathbf{I}(t) = \mathbf{I}_0 + \sum \mathbf{A}_i \bullet \exp\left(-\frac{t}{\tau_i}\right) \tag{1}$$

Here, I_0 is the contribution of background level describing the role of slow components. A_i amounts the amplitude maximum of each exponential component with τ_i as lifetime. Fig. 1 (b) is devoted to luminescence decay kinetics of d - f emission bands of samples presented in Fig. 1 (a). The XRL decay curve of KLuP₂O₇ demonstrates nearly single exponential decay behaviour without any noticeable build-up stage with lifetime of 18.4 ns. The d - f emission decay kinetics of K₃Lu(PO₄)₂ is well fitted by exponential approximation with parameters: $\tau \sim 15$ ns for sample with 5% Pr^{3+} and $\tau \sim 20.5$ ns for sample with 1% Pr^{3+} . Sr₉Sc (PO₄)₇ reveals a fast component ($\tau \sim 15$ ns) while the contribution of the slow µs decay component reaches 18%. Decay kinetics of LiSrPO4 is very same as in KLuP₂O₇, and it is described with same lifetime of 18 ns. From presented kinetics the only material with noticeable build-up stage is Sr₉Sc(PO₄)₇. We suppose that presence of this stage is caused with defect-related luminescence and energy transfer from impurity ions to host defects. The observed $Pr^{3+} 4f^15d^1 - 4f^2$ emission lifetime of the

main decay component is consistent with that documented for some other Pr^{3+} -doped phosphates.

3.2. Electron beam irradiation

Recordings of luminescence spectra were done with pure samples and after irradiating with fast electrons (E = 10 MeV) using the linear electron accelerator. To avoid heating of crystal structure under radiation beam, we used an existing conveyor system with partial irradiation doses of 11 kGy. Absorbed dose is controlled with film dosimeters. For irradiation time of ~4 s, induced optical density was measured at 550 nm wavelength. Attested film dosimeter SO PDE-1/50 "VNIIFTRI" (for absorbed dose 1–50 kGy region) was used. Using this system, samples were irradiated during several seconds, then they moved through conveyor circle for approx. 30 mins. This system allowed not to heat samples to avoid destroying of new defects through thermally stimulated luminescence mechanism. For all samples measurements have been performed for 15 and 30 cycles.

When the crystal interacts with heavy ions flux, arriving particles would cause cascade of atoms offsets inside of lattice. Electrons with energy more than 1 MeV would generate point defects along distribution trajectory. Most of appearing defects would be stable, during lifetime they are able to diffuse deeper in material and recombine with interstitial atoms if such interaction is energy-allowed. The more is the energy of electrons the deeper they can enter the material and form the defect.

Before discussing the results of the experiment, authors would provide theoretical evaluation of absorbed dose value. All data in this report correspond to official certified dose measurement, but since studied samples are powders and are rather thin, one should understand that real dose is less. For example, let authors try to analyse dose in K₃Lu (PO₄)₂:Pr³⁺ (1%) ($\rho = 3.9$ g/cm³, $Z_{eff} = 44.5$) [16].

First, linear energy losses and maximum mileage were analysed using Bethe formula (2) and Kanaya-Okayama (3) [20] experimental expression for electrons:

$$\frac{dE}{dx} = -\frac{7.85 \bullet 10^4 \bullet Z_{eff} \bullet \rho}{A \bullet E_0} \bullet \ln \frac{b \bullet E_0}{\overline{I}},$$
(2)

$$R = 0.0276 \frac{A \bullet Z_{eff}^{-8/9}}{\rho} \bullet E_0^{\frac{5}{3}}$$
(3)

Here *A* – average molar mass of the material, b = const = 1.166, E_0 – electron energy, \bar{I} – average energy of the excited atom. Thus, $\frac{dE}{dx} = 28.1$ MeV/cm, R = 3.64 cm. Thickness of studied sample is much less than



Fig. 2. (a): PL spectra of KLuP₂O₇:Pr³⁺ (1%) upon UV excitation (E_{exc}), before (black) and after irradiation (red, green) with 10 MeV electrons. (b): PL excitation spectra of KLuP₂O₇:Pr³⁺ (1%) of emission bands (E_{emis}), before (left) and after irradiation (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 3. (a): PL spectra of $Sr_9Sc(PO_4)_7$, Pr^{3+} (1%) upon UV excitation (E_{exc}), before (black) and after irradiation (red) with 10 MeV electrons. (b): PL excitation spectra of $Sr_9Sc(PO_4)_7$, Pr^{3+} (1%) of emission bands (E_{emis}), before (left) and after irradiation (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

maximum mileage of the electron on this material. So, only small part of electrons energy will be absorbed by the sample. Samples are 0.2 mm thick, round-formed with radius of 0.5 cm. Thus, linear energy loss of one electron here would be 562 keV.

To make the conclusion about absorbed dose one should count number of interactions between material and flux. According to Ref. [21], we would use 10 kW as outer power of the flux. Then, for samples of our size, number of interactions would be $\sim 10^{12}$. Thus, common energy losses in sample would be $5.5 \cdot 10^{14}$ eV, or 0.034 J. With such energy losses, value of absorbed dose is 650 Gy for 1 s. With average time of flux irradiation of ~4 s, we get 2.6 kGy per cycle. So, total absorbed dose will be determined by number of cycles and will be from 40 to 80 kGy, which is 4 times less than dosimeter data.

The object of the experiment is to research defects existence and their role in optical properties of studied samples after electron irradiation. In general, electrons can interact with crystal lattice of solid states in three various scenarios: deceleration, scattering and absorption. These processes are described with different mechanisms of elastic and inelastic collisions. From defects point of view, ionization of electron shells of the crystal and elastic collisions of fast particles with nucleus of lattice atoms could be a reason of point defects radiation formation. In case of less electron energy electron fluxes would not be able to transport energy enough for defects formation, so their interaction will be described with phonon generation or with elastic scattering mechanism resulting in changing electron trajectory.

So, while irradiating the samples we suppose to observe two mechanisms of radiation formation of point defects: impact mechanism – elastic collisions of fast particles with nucleus of lattice atoms, and ionization mechanism – excitation of electron shells of the crystal and their ionization. Structural radiation defects in solids are usually Frenkel defects. They can appear from both mechanisms – either by atom moving from regular node after collision with accelerated particle or after disturbance of electron subsystem. Besides structural defects, one is supposed to find ionized during irradiation radicals' groups which are formed by phosphorus and oxygen in observed samples.

Fig. 2 (a) presents PL spectra of KLuP₂O₇:Pr³⁺ (1%) recorded upon UV excitation at room temperature (RT). The broad UV emission bands dominating in the PL spectra correspond to the parity-allowed interconfigurational radiative transitions from the lowest excited $4f^15d^1$ state to multiplets of the ground $4f^2$ electronic configuration of the Pr³⁺ ion. No f - f emission lines are observed. Defect-related luminescence is presented by a broad emission band spread from 350 to 600 nm with maximum near 450 nm. With irradiation one can easily determine the redistribution of interconfigurational transitions. Trend for changing is following: both peaks of d-f transitions have become equal in intensity, but definitely divided from one another. Then, with dose increasing (green) these two peaks lose their separateness and become one wide band with maximum at 265 nm.

Behaviour of defect–related luminescence changes more drastically. Pure sample demonstrates one–peak (maximum at 415 nm) band with low relative intensity, but after irradiation (red) form of this band becomes more complex. It grows in intensity, divides in two peaks (with maxima at 425 and 540 nm) with almost equal intensity but 425 nm peak dominates a little. With further irradiation (green) defect–related luminescence still is presented with two bands though their peaks and intensity changes. Now these peaks have maxima at 460 and 580 nm and latter dominates.

PL excitation spectra recorded monitoring different emission bands (E_{emis}) are presented in the Fig. 2 (b). Excitation features related to intracenter $Pr^{3+} 4f^{1}5d^{1} - 4f^{2}$ transitions are observed as a broad complex band in the UV region between 200 and 250 nm. The excitation spectrum recorded for the emission band located at 450 nm demonstrates a feature near 5 eV that is followed by a further increase of the excitation efficiency while scanning the spectrum towards upper energy limit of 6 eV. PL excitation spectra (Fig. 2 (b)) demonstrate the most effective excitation at 5.5 eV. These spectra indicate that we observe not direct excitation of defects, but efficient energy transport from impurity centers to defects of crystal lattice.

PL spectra of Sr₉Sc(PO₄)₇.Pr³⁺(1%) are presented in Fig. 3 (a). This spectrum is dominated with bands of d - f transitions in 250–300 nm area, and two other ways of emission are hardly observed. d - f band is a set of two peaks with different intensity. Peak with higher energy dominates in spectrum.

After irradiation, it can be easily observed that d - f transitions are redistributed and become equal. More interesting for discussion here is the behaviour of defect–related luminescence. The first feature is the fact that defect–related luminescence actually appears. So, we observe presence of defects formed by phosphorus and oxygen, same as in previous sample. Similar position of bands maxima confirms this suggestion. The second feature estimates the dependence of emission level from absorbed dose. Red spectrum responds 160 kGy, and green – 320 kGy. It is well observed that defect–relative luminescence band becomes more intensive and redistributes peaks intensity. In both spectra two bands' maxima are observed: 455 and 570 nm. 455 nm, as



Fig. 4. (a): PL spectra of $K_3Lu(PO_4)_2$: Pr³⁺ (1%) upon UV excitation (E_{exc}), before (black) and after irradiation (red, green) with 10 MeV electrons. b) PL spectra of $K_3Lu(PO_4)_2$: Pr³⁺ (5%) upon UV excitation, before (black) and after irradiation (red) with 10 MeV electrons. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. (a): PL excitation spectra of $K_3Lu(PO_4)_2$: Pr^{3+} (1%), before (left) and after irradiation (right). (b): PL excitation spectra of $K_3Lu(PO_4)_2$: Pr^{3+} (5%), before (left) and after irradiation (right).

higher–energy band, increases its intensity while 570 nm line has no significant gain.

PL excitation spectra of $Sr_9Sc(PO_4)_7$.Pr³⁺ (1%) are dominated with the broad complex band with maximum at 5.15 eV. It can be observed that after irradiation increases relative intensity of every emission energy spectrum. This fact proves ideas about lattice and electrons interactions – electron beam would form additional centers adding their contribution in overall spectrum.

Fig. 4 (a) and (b) contains PL spectra of $K_3Lu(PO_4)_2:Pr^{3+}$ (1% and 5%). It is well observed that relative intensity of d - f transitions increases above defect luminescence level. Both 1% and 5% samples present defect–related luminescence bands. At 1% impurity level this band has two divided peaks with maxima at 450 and 550 nm, and at 5% – one–peak (490 nm) wide band. In 1% sample with irradiation defect–related luminescence drops, loses its peaks and forms flat plateau. This measurement allows to conclude that sample irradiation can make possible to manage the channel of excitation – e.g., to decrease defect–related luminescence. Probably, defects that are formed under irradiation are small charge carriers' traps to detect which study of thermally stimulated processes is needed. The fact is that in room temperature conditions irradiation samples act as scintillators with one main emission channel, and this channel are interconfigurational d - f transitions. Such samples are more convenient in use – it is a fast narrow-

band emitter.

PL excitation (Fig. 5) underlines most effective energy transfer towards interconfigurational mechanism of emission. It is worth to be mentioned that tends of intraconfigurational f - f transitions are not observed in both centers what is approved by theory [1] where is declared that materials with Stokes shift less than 3200 cm⁻¹ will be dominated in PL spectra with interconfigurational d - f transitions.

4. Conclusions

In summary, irradiation of studied objects with 10 MeV electrons influences on their spectroscopic properties. The new ratio of emission levels is observed, the effectiveness of energy transport changes. New emission bands can be seen in Sr₉Sc(PO₄)₇:Pr³⁺ (1%) and KLuP₂O₇:Pr³⁺ (1%). Before irradiation there were only weak tends of defect–related luminescence, most probably formed by crystals growth process. Irradiation with electron beam results in formation of new emission centers. We can observe defect–related radiative band in both samples with maxima in similar positions. This fact allows to suppose that reason for such transitions could be interaction of electrons with radical groups of phosphorus and oxygen. Probably, such centers can have a formula of (PO₂)²⁻ or (PO₃)²⁻ which were observed in other lattices. For further investigation measurements of EPR spectra are needed. The second

variant of interacting is observed in $K_3Lu(PO_4)_2:Pr^{3+}$ (1% and 5%) spectra. Here, most probably, irradiation does not form new centers – it is observed, that in contrary, it "suppresses" defect–related bands. In both samples it is well seen, that while d - f peak does not change, relative intensity of defect–related luminescence falls with absorbed dose increasing. Thus, e-beam irradiation modifiers existing defects.

As it can be concluded from PL spectra, with selective excitation and generation of charge carriers, an effective energy transfer from electron excitations towards both impurity centers and defects. In Sr₉Sc (PO₄)₇.Pr³⁺ (1%) and KLuP₂O₇:Pr³⁺ (1%) impact of energy transfer towards defects is rather high, so channel of charge carriers capturing on the defects practically suppresses channel of their energy transfer on excited $4f^{1}5d^{1}$ -state of Pr³⁺-ions. In contrary, in K₃Lu(PO₄)₂:Pr³⁺ (1% and 5%) spectra after irradiation it is well observed that dominant channel of energy transfer are impurity centers not defects. The fact is that in room temperature conditions irradiated samples act as scintillators with one main emission channel, and this channel are interconfigurational d-f transitions. Such samples are convenient in use, as it is easier to construct detector system around narrow–band emitter.

Further investigation of optical properties management is supposed to be performed both increasing absorbed dose got by electron beam irradiation and after interacting with neutron fluxes. Phosphorous groups are supposed to demonstrate a significant susceptibility towards this type of irradiation.

Credit author statement

S.A. Kiselev: Conceptualization, Funding acquisition, Data curation, Writing- Reviewing and Editing. V.A. Pustovarov: Methodology, Investigation, Validation, Writing – original draft, Writing- Reviewing and Editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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