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The white light caused by defects and complex cation distribution in ZnAl$_{2-x}$Fe$_x$O$_4$ magnetic nanocrystals

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Abstract

ZnAl$_2$O$_4$ with spinel structure has attracted more attentions due to its robust dielectric and luminescence properties. Complex cation distribution in spinel structure influences the optical and magnetic properties. Herein, we report white emission related to the defects and the magnetism assigned to Fe impurity in ZnAl$_{2-x}$Fe$_x$O$_4$ (0 ≤ x ≤ 0.6) nanocrystals fabricated by using common sol-gel method at a relatively lower temperature (700 °C) than that reported earlier. ZnAl$_{2-x}$Fe$_x$O$_4$ phosphors reveal single spinel phase without impure phase. Complex cation distribution is observed in all samples, for instance, Fe and Zn in antisites, cation vacancies, and with Fe content increasing, cation distribution reveals obvious change. The band gap energy of ZnAl$_{2-x}$Fe$_x$O$_4$ phosphors is reduced from 3.84 eV to 3.33 eV when the content of Fe ions (x value) increases from 0 to 0.6. Two wide band emissions assigned to the various types of shallow and deep donor/acceptor defects are observed, monitoring with the excitation wavelength of 280 nm. The Commission International de l’Eclairage (CIE) colour coordinate (x, y) of the ZnAl$_{2-x}$Fe$_x$O$_4$ phosphors is found to shift from (0.3218, 0.2957) to (0.3422, 0.3122) with Fe doping in spinel lattices owing to rearrangement of defects, indicating the potential application in white-light illumination. ZnAl$_{2-x}$Fe$_x$O$_4$ reveals a room ferromagnetism resulting from Fe$^{3+}$ ions in spinel lattices.

1. Introduction

Ceramics based on zinc aluminate (ZnAl$_2$O$_4$) have attracted more attentions due to their wide potential applications in the field of catalysis, energy storage, dielectric ceramics, light emitting diodes (LED) and so on [1–5]. Different from ZnO, TiO$_2$ and organic materials, ZnAl$_2$O$_4$ (ZAO) crystals have higher mechanical resistance, thermal stability and acid-alkali resistance, which causes that ZnAl$_2$O$_4$-based devices can maintain the excellent physical and chemical performances in poor conditions. Due to the wide band gap (E$_g$ = 3.8 eV), the emitting wavelength can be tuned by rare earth or transition elements, such as Eu, Tb, Dy, Mn, Ti and so on, doping in zinc aluminate crystal lattices [6–8]. Rare earth doped ZAO has been investigated widely due to the high efficiency of rare earth exciting centres. Considering the economic factor, more and more investigations focusing on the luminescence of transition metals as the substitutes of rare earth have been carried out. A green emission can be excited in Mn$^{2+}$-doped ZAO phosphors, blue emission can be observed in Ti$^{3+}$-doped ZAO phosphors, and red emission is detected in Cr$^{3+}$-doped ZAO, and so on. In the reports of Pathak et al. [9], a series of blue and near infrared emissions were observed in Fe$^{3+}$-doped ZAO nanophosphors.

ZnAl$_2$O$_4$ is a normal spinel with space group, $Fd3m$. Zn$^{2+}$ ions occupy the centres of oxygen tetrahedron and Al$^{3+}$ occupy the centres of oxygen octahedron as shown in figure 1. The dopants with different valences should occupy the corresponding sites, tetrahedral centres (+2) or octahedral centres (+3). It is reported that Mn$^{2+}$ ions tend to occupy Zn$^{2+}$ sites, emitting a green light, and Mn$^{3+}$ or Mn$^{4+}$ ions tend to occupy Al$^{3+}$ sites, emitting a red light [10, 11]. However, some defects are easily formed in ZAO spinel lattices because of higher
synthesized temperature. The results of previous studies show that the oxygen vacancies are the main defects [12], and the interstitial ions and inversion ions coexist in spinel lattices normally. In general, Cr\(^{3+}\) ions occupy the octahedral centres (Al\(^{3+}\) sites) in order to balance the valence, and a narrow emitting peak at 687 nm assigned to \(^{2}E_{2g} \rightarrow ^{2}A_{2g}\) (R line) is excited [10]. However, some Cr\(^{3+}\) ions can occupy the tetrahedral centres (Zn\(^{2+}\) sites) and some inversion defects related to octahedral Zn and tetrahedral Al are formed when the synthesized temperature is higher than 500 \(^\circ\)C, which changes the crystal field around Cr\(^{3+}\) ions and results in the shift of \(^{2}E_{2g}\) level, as a result, a new peak at 698 nm (N line) can be excited [13, 14]. The general methods to synthesize the spinel structure of ZAO are sol-gel method and solid phase method [5, 15–17], and the synthesized temperature is higher than 1000 \(^\circ\)C which causes the more inversion defects in spinel lattices. In order to investigate the crystalline and the defects in ZAO crystals, more and more researches are focused on the methods to fabricate the ZAO crystals at low temperature, such as solvothermal method and microwave method [18]. But the solvothermal method is unsuitable to synthesize the ZAO crystals doped with multi-impurities. So the sol-gel method is still a popular method. Due to the excellent dielectric properties, Fe\(^{3+}\) doped ZAO has been attracted more attentions. Furthermore, a blue emission band and a near-infrared (NIR) emission band assigned to Fe\(^{3+}\) in ZAO lattices were reported, which were assigned to tetrahedral Fe\(^{3+}\) and octahedral Fe\(^{3+}\) respectively [9, 16, 19, 20]. While there are few studies about the influence of Fe dopants on the structure, optical and magnetic properties and the defects in ZAO crystals.

In this paper, we fabricated Fe\(^{3+}\)-doped ZnAl\(_2\)O\(_4\) nanophosphors using sol-gel method, and observed visible white light under ultra violet (UV) excitation. The structural, optical and magnetic properties of ZnAl\(_{2-x}\)Fe\(_x\)O\(_4\) are investigated.

2. Materials and methods

2.1. Materials
The precursor materials were zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\)·6H\(_2\)O), aluminum nitrate nanahydrate (Al(NO\(_3\))\(_3\)·9H\(_2\)O), iron chloride hexahydrate (FeCl\(_3\)·6H\(_2\)O) and ethylene glycol were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. All the chemicals were analytical reagent and were used as starting materials without further purification.

2.2. Synthesis of ZnAl\(_{2-x}\)Fe\(_x\)O\(_4\) phosphors
The theoretical composition of ZnAl\(_{2-x}\)Fe\(_x\)O\(_4\) phosphors were prepared by common sol-gel process, where \(x\) = 0, 0.1, 0.2, 0.3, 0.4 and 0.6, respectively. Stoichiometric quantities of Al(NO\(_3\))\(_3\)·9H\(_2\)O, Zn(NO\(_3\))\(_2\)·6H\(_2\)O and FeCl\(_3\)·6H\(_2\)O were dissolved in mixtures of deionized water and ethylene glycol, and were stirred continuously to obtain the uniform sols. Then the transparent sols were kept at 180 \(^\circ\)C in oven for about 4 h until became puffed gelation. At last, the puffed products were calcined to obtain ZnAl\(_{2-x}\)Fe\(_x\)O\(_4\) nanophosphors at 700 \(^\circ\)C, and the sintering time was 2 h. The details were similar with our previous work [21, 22].

2.3. Characterizations
The phase and crystalline nature of the obtained products was characterized using both x-ray diffractometer with Cu- K\(\alpha\) radiation (\(\lambda\) = 0.15406 nm). The morphologies were characterized by using JEM-2000EX type transmission electron microscope (TEM). The room absorption spectra were measured by using Shimadzu UV
2700 type UV–visible spectrophotometer. The x-ray photoelectron spectroscopy (XPS) analysis was carried out with a Thermol scientific Escalab 250Xi using monochromatized Al Kα x-ray source (hν = 1486.6 eV, 150 W, diameter beam spot: 500 μm). The PL spectra were measured with Edinburgh Instruments FLS920 type Spectro-fluorophotometer, and 450W Xe-lamp was used as the exciting light source. The magnetic hysteresis loops of the films were measured by Lakeshore 7404 vibrating sample magnetometer (VSM) with the sensitivity of 0.1 × 10⁻⁶ emu at room temperature.

3. Results and discussions

3.1. Structural properties

The x-ray diffraction (XRD) patterns of ZnAl₂₋ₓFeₓO₄ nanophosphors are shown in figure 2(a). All diffraction peaks are assigned to the spinel structure of zinc aluminate crystals, and no impurity phases are observed, indicating that Fe atoms enter the spinel lattices of zinc aluminate. It is well known that Fe³⁺, Al³⁺ and Zn²⁺ ions have different radium which is 0.645 Å for Fe³⁺, 0.54 Å for Al³⁺ and 0.74 Å for Zn²⁺, respectively. Impurities, such as dopants, vacancies, interstitial and antisite defects, should result in the shift of Bragg angle. When the ions with larger radius are replaced by the ions with smaller radius, the Bragg angle should be enhanced. If the ions with smaller radius are replaced by the ions with larger radius, the Bragg angle should decrease. It is noted that the Bragg angle decreases firstly and then increases with the content of Fe³⁺ ions increasing as shown in figure 2(b). The decreasing Bragg angle indicates that the Fe³⁺ ions should trend to replace the Al³⁺ ions, while the increasing angle indicates that Fe³⁺ ions occupy the octahedral site of Zn (related to the inversion defects), and should result in the decrease of inversion defects. So the shift of Bragg angle suggests the redistributions of positive ions in spinel lattices.

The crystallinity of ZnAl₂₋ₓFeₓO₄ crystals should be described by using mean crystallite size. In general, the larger crystallite size indicates the better crystallinity. The mean crystallite size can be evaluated by using Scherrer’s equation as follows [23]:

\[ G = \frac{0.9 \lambda}{\beta \cos \theta} \]  

Where G is the mean crystallite size, \( \lambda \) is the wavelength of x-ray, \( \beta \) is the full width at half maximum, and \( \theta \) is Bragg angle. The calculated values of mean crystallite size are shown in figure 2(c). With the contents of Fe³⁺ ions increasing, the crystallite size reveals an obvious increase, and is stabilized when \( x > 0.3 \).

3.2. Morphologies

The morphologies of ZnAl₂₋ₓFeₓO₄ nanophosphors were characterized by TEM and high resolution transmission electron microscopy (HR-TEM), and the results are shown in figure 3. With Fe doping in ZnAl₂O₄, the crystallite size reveals an increase, corresponding to the results of XRD.

3.3. X-ray photoelectron spectroscopy

XPS is an effective technology to detect the state change of transition metal ions in inorganic compounds synthesized in various conditions. The tetrahedral and octahedral sites in spinel lattices for Zn²⁺, Al³⁺ and Fe³⁺ ions can be distinguished in XPS spectra because of the large difference in binding energies. Zn, Al, Fe and O
elements are detected in ZnAl$_2$-Fe$_x$O$_4$ particles as shown in figure 4(a). In order to confirm the structure of ZnAl$_2$-Fe$_x$O$_4$ crystals, the high-resolution XPS curves are measured. Figure 4(b) shows the high-resolution XPS spectra in Al2p region of ZAO crystals doped with various concentrations of Fe$^{3+}$ ions. The signal peak can be fitted well with single Gaussian lineshape, which is assigned
to the octahedral Al [24, 25]. With the concentration of Fe$^{3+}$ ions increasing, the single peak reveals a tiny shift from 74.68 eV to 74.47 eV, indicating that the chemical atmosphere is changed. The tetrahedral Al (Al$^{2+}$) is not detected in the surface lattices for these samples.

A spin doublet for Zn$^{2+}$/2 and Zn$^{2+}$/2 at about 1022 eV and 1045 eV are detected as shown in Figure 5. Every signal peak can be fitted well with two Gaussian lineshapes, indicating that the inversion defects exist in ZnAl$_2$O$_4$ lattices [26]. It is noted that the intensity of the fitted peaks associated to the octahedral Zn decreases, indicating that the inversion defects related to octahedral Zn decrease with Fe$^{3+}$ ions doping in spinel lattices.

For all samples, the Fe element is characterized by a spin-coupled doublet Fe$^{2+}$/2 and Fe$^{2+}$/2 at about 712.0 eV and 725.9 eV, respectively, and two satellite peaks with binding energies approximately about 7 eV higher than the corresponding Fe$^{2+}$ peaks as shown in Figure 6. The signal peaks associated to Fe$^{2+}$/2 and Fe$^{2+}$/2 are fitted well with two Gaussian lineshapes, indicating that the octahedral Fe and tetrahedral Fe exists in zinc aluminate crystals. The Fe$^{2+}$/2 peak at about 711.9 eV is assigned to the octahedral Fe (Fe$^{3+}$/2) in spinel lattices, and that at higher binding energy about 712.5 eV is assigned to the tetrahedral Fe (Fe$^{3+}$/2) in spinel lattices [21].

With the concentration of Fe increasing, the relative intensity of signal peak associated to Fe$^{3+}$/2 decreases and that associated to Fe$^{3+}$/2 increases. Due to the same valence for Fe$^{3+}$ and Al$^{3+}$ ions, Fe$^{3+}$ ions tend to occupy the octahedral sites in spinel lattices. The radius of Al$^{3+}$, Fe$^{3+}$ and Zn$^{2+}$ is 0.54 Å, 0.65 Å and 0.74 Å, respectively. Octahedral Fe results in the stress in spinel lattice due to the larger radius of Fe$^{3+}$ than that of Al$^{3+}$, which should induce the larger stress in whole zinc aluminate crystals with Fe content increasing. While tetrahedral Fe causes the strain in spinel lattice due to the smaller radius of Fe$^{3+}$ than that of Zn$^{2+}$, which can reduce the stress in whole crystals.

Due to the octahedral Zn and tetrahedral Zn coexisting in ZAO spinel lattices, the observed octahedral Fe occupies not only the site of octahedral Al, but also the site of octahedral Zn, which reduces the content of octahedral Zn corresponding to the XPS results of Zn. Furthermore, Fe ions occupy the site of Al and Zn in spinel lattices, which is the reason why the Bragg angle decreases and then increases with Fe$^{3+}$ ions content increasing as shown in Figure 2(b).
3.4. Optical properties

The absorption spectra of ZnAl$_{2-x}$Fe$_x$O$_4$ crystals are shown in figure 7. Three absorption bands are detected at about 460 nm, 320 nm and 274 nm, respectively. With the Fe$^{3+}$ dopants increasing, the absorption is enhanced ranging from 200 nm to 800 nm. The absorption bands at 274 nm, 320 nm and 460 nm are assigned to Al-O, Zn-O and Fe-O groups, respectively. The band gap energy ($E_g$) can be evaluated from absorption spectra by using the following formula [27]:

$$ (\alpha h\nu)^2 = A(h\nu - E_g) $$

Where $h\nu$ is the photon energy. The corresponding plots of $(\alpha h\nu)^2$ vs. $h\nu$ are shown in figure 8. For the pure zinc aluminate crystals, the band gap energy is 3.84 eV which is similar with that of bulk zinc aluminate crystals (about 3.8 eV). With the Fe$^{3+}$ ions increasing, the band gap energy reveals an obvious decrease from 3.84 eV to 3.33 eV. When the metal oxide ion of low band energy added to other materials of high band energy, the produced new materials should have a new band gap with a value between the two materials, and the observed decrease in band gap energy with Fe$^{3+}$ doping in ZAO could be attributed to the formation of new states at lower energy due to the defects existing in the phosphors [28–30].

The PL spectra of ZnAl$_{2-x}$Fe$_x$O$_4$ phosphors are detected and the results are shown in figure 9. Two wide emitting bands centred at about 430 nm and 610 nm are observed for all samples. A blue band centred at about 450 nm from tetrahedral Fe$^{3+}$ and a red band centred at about 710 nm from octahedral Fe$^{3+}$ are reported by Pathak et al [9]. While the blue emission at 430 nm and the red emission at 610 nm are observed in the pure zinc aluminate phosphors without Fe$^{3+}$ dopants in our samples, indicating that these emission bands should not come from Fe$^{3+}$ ions in current phosphors. According to the results of XRD and XPS, these emissions should be resulted from the defects in spinel lattices. Furthermore, it is noted that the relative intensity between blue and red bands reveals an obvious decrease with Fe$^{3+}$ contents increasing as shown in the insert in figure 9. It suggests that the defects existing in spinel lattices are tuned by Fe$^{3+}$ dopants. Cornu et al [31] reported the similar emissions in ZAO spinel powders which emissions depend on the annealing temperature strongly. In their report, the wide emission bands centred at 460 nm and 610 nm were observed in ZAO powders synthesized at
1200 °C under measurement temperature of 254 k, and were attributed to the interstitial zinc ions (Zni, 460 nm) and oxygen vacancies (VO, 610 nm), respectively. In the reports of Pathak et al [32], the emission bands centred at 430 nm, 700 nm and 840 nm were separated with various peaks contributed to various defects in spinel lattices. In our samples, the change in the relative intensity of blue and red emissions indicates that the defects should be changed with Fe³⁺ dopants increasing, and the emission bands are too wide to be only assigned to single kind of defects.

In order to analyse the origin of these emissions furtherly, the PL curves are fitted with Gaussian lines and the results are shown in figure 10. It is obvious that all curves are fitted well with multiple Gaussian lines at 436 nm.

**Figure 8.** Square of the absorption coefficient as a function of photo energy for ZnAl₂₋ₓFeₓO₄ phosphors. (a) x = 0; (b) x = 0.2; (c) x = 0.3; (d) x = 0.6.

**Figure 9.** PL spectra of ZnAl₂₋ₓFeₓO₄ phosphors.
The probable defects exist in samples are grouped into three categories: shallow donor defects viz. $\text{Al}^+$, $\text{Zn}^+$, deep band gap defects viz. $\text{V}_\text{O}^-$, $\text{O}^+\text{V}_\text{O}^-$, $\text{V}_\text{O}^2-$ and shallow acceptor defects viz. $\text{V}_{\text{Zn}}$ and $\text{Zn}^-\text{Al}^+$ [33]. The inversion defects of $\text{ZnAl}^+$ could be neutralized due to the capture of a free hole with high irradiation, which causes the electron transition from donor level to acceptor level of $\text{ZnAl}^+$ (near the valence band ($\text{VB}$)). The inversion defects of $\text{AlZn}^+$ can also capture a free electron and form a new donor level near the conductor band ($\text{CB}$), but the captured electron may leave its trap and recombine with a near trapped hole due to the lower electron affinity of $\text{Al}^{3+}$ ions [33]. Due to the capture of free electrons and holes in the spinel lattices, the defects related to $\text{V}_{\text{O}}^-$, $\text{V}_{\text{Zn}}^-$, $\text{Zn}^-\text{Al}^+$ are partially transformed into the defects related to $\text{V}_{\text{O}}^+$, $\text{V}_\text{O}^-$, $\text{V}_{\text{Zn}}^-$, $\text{V}_{\text{Al}}^2$ and so on, and some new level in band energy gap could be formed. These defects cause the complex energy levels and multiple emission peaks in zinc aluminate crystals.

The probable electron transition of various emission components is shown in figure 11(a). Oxygen vacancies usually exist in oxide compounds due to the lowest enthalpy of formation as well as ease of generation during vigorous combustion of reaction, contributing to the red or near infrared emissions [33], as a result, the emissions observed in current samples should be related to oxygen vacancies. The cyan emission at 489 nm is attributed to the $\text{CB} \rightarrow \text{L}_8$ transition and the red emission at 610 nm is attributed to the $\text{L}_4 \rightarrow \text{VB}$ transition. The contents of octahedral $\text{Zn}$ are reduced with $\text{Fe}^{3+}$ dopants increasing as shown in the results of XPS, and the recombination of $\text{Zn}_{\text{Al}}^-\text{Al}^+$ and $\text{V}_{\text{O}}^+$ decreases the $\text{Zn}_{\text{Al}}^-\text{Al}^+$ acceptors and $\text{V}_{\text{O}}^+$ donors furtherly, which causes the intensity of cyan emission decreasing even vanishing. Furthermore, the increasing in the content of $\text{V}_{\text{O}}^-$ defects due to the recombination of $\text{Zn}_{\text{Al}}^-\text{V}_{\text{O}}^-$ pairs enhances the red emission of 610 nm attributed to the $\text{L}_4 \rightarrow \text{VB}$ transition. The electron and hole recombination of these defects enhances the probability of electron transition between the levels related to oxygen vacancies, which causes that the relative intensity of these emissions

**Figure 10.** PL spectra (black lines) and the fitted curves of ZnAl$_{2-x}$Fe$_x$O$_4$ phosphors. $x =$ (a) 0; (b) 0.1; (c) 0.2; (d) 0.3; (e) 0.4; (f) 0.6.
assigned to the oxygen vacancies increases, such as P2, P4, P5. The increase of electron transition from L2 to L5 and from L3 to L7 should reduce the transition from L2 to L7, causing the intensity of P1 decreasing.

Figure 11(b) shows the Commission International De l'Eclairage (CIE) diagram of ZnAl_{2-x}Fe_{x}O_{4} phosphors under 280 nm excitations. The CIE colour coordinates (x, y) of the ZnAl_{2}O_{4}:Fe^{3+} crystals are calculated by using the fluorescence spectra. The CIE colour coordinate (x, y) of the ZnAl_{2}O_{4}:Fe^{3+} crystals is found to shift from (0.3218, 0.2957) to (0.3422, 0.3122) with the concentration of Fe^{3+} ions increasing because of the changing relative intensity between blue and red emissions. The white emission image is recorded and a visible white emission is observed as shown in the insert of figure 11(b). So zinc aluminate can be applied in LED field as a kind of potential luminescent material.

According to the above analysis, the change of PL mainly comes from the decrease of Zn_{i} and the increase of V_{O}. When the Fe^{3+} ions enter the spinel lattices, the cations reveal redistribution. As shown in the results of XPS, Fe^{3+} ions occupy the octahedral and tetrahedral sites in spinel lattices, and Fe-O is easily formed because Fe is more active than Zn and Al, which causes more Zn-V_{O} formed and new unbalance of charges in spinel lattices. So various emissions can be observed as shown in figure 10.

3.5. Magnetic properties

The room ferromagnetism of ZnAl_{2}O_{4}:Fe^{3+} phosphors is detected and the hysteresis loops are shown in figure 12. It can be seen that the pure zinc aluminate powders show the diamagnetism corresponding to the previous reports [8, 34]. With diluted Fe^{3+} doping in lattices, zinc aluminate phosphors reveal ferromagnetism. Fe^{3+} is a kind of magnetic ions with 3d^{8} state which value of magnetic moments is 3.79 \mu_{B} in spinel lattices [19]. In the inverse spinel lattices, the magnetic moments of Fe^{3+} ions in octahedral sites are antiparallel with that of
Fe$^{3+}$ ions in tetrahedral sites, inducing that the ferromagnetism comes from the magnetic moments of Fe$^{3+}$ ions occupying the octahedral sites. In the spinel structure of zinc aluminate crystals, Fe$^{3+}$ should tend to occupy the octahedral sites (Al sites) due to balancing valence and the similar ions radius with Al$^{3+}$ ions. With the dilute Fe$^{3+}$ doping in ZnAl$_2$O$_4$ lattices, the magnetism of zinc aluminate crystal should be affected by the magnetic moments of Fe$^{3+}$ ions, as a result, the zinc aluminate should reveal magnetism at room temperature.

Furthermore, the results of PL indicate that there are many oxygen vacancies existing in ZAO lattices. The results from Abu El-fadl [20] indicate that the interaction between the ions and $V_O$ can cause the room temperature magnetism. Considering this reason, the Fe-Vo should be another origination of the magnetism.

4. Conclusions

Pure spinel phase of zinc aluminate phosphors doped with various contents of Fe$^{3+}$ ions was fabricated successfully by sol-gel method. Fe$^{3+}$ ions induced redistribution of cations in spinel lattices. Fe$^{3+}$ ions trend to occupy the octahedral sites due to the same valence as that of Al$^{3+}$ ions, and the antisite defects of octahedral Zn are reduced with Fe$^{3+}$ dopant contents increasing. The redistributions of cations in spinel lattices caused new unbalance of charges and defects, which resulted in various wavelengths of visible light assigned to the oxygen vacancies, intersistial Zn, antisite defects and their recombination in spinel structure, and the visible white light can be observed. The diamagnetic zinc aluminate is conversed to ferromagnetic material with Fe$^{3+}$ dopants.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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