Luminescent properties of blue-emitting long afterglow phosphors $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x = 0, 1$)

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Abstract

The luminescence of two newly developed blue-emitting long afterglow phosphors, $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x = 0, 1$), has been studied. The emission under VUV–UV excitation from a synchrotron radiation source, along with the long afterglow spectra have been measured at different temperatures ranging from 7 to 300 K. While the emission spectra under 170 nm excitation exhibit both the 5d–4f transitions of Eu^{2+} and 4f–4f transitions of Dy^{3+} , only the blue band corresponding to the 5d–4f transitions of Eu^{2+} is observed in the long afterglow spectra. Emission of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ excited by an intense VUV laser source (157.6 nm) is also reported. The rich line structures in the laser-excited emission spectra partly result from 4f–4f transitions of Eu^{3+} , indicating an efficient photon-induced process, which promotes Eu^{2+} to Eu^{3+} . The thermoluminescence covering the temperature range from 50 to 450 K for both samples has been measured as well and the depth of the traps responsible for the long afterglow emission was estimated. The mechanism of the persistent luminescence and the origin of the traps are discussed in the light of these results.

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1. Introduction

The long afterglow phosphors are a special kind of luminescent materials with long persistent phosphorescence lasting for several hours at room temperature. As novel functional materials, these

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long afterglow phosphors are drawing more and more attention in recent years because of a constantly growing market for their applications in traffic signs, emergency signage, watches and clocks, textile printing, among others [1,2]. As a new generation of long afterglow phosphors, lanthanide ion doped alkaline earth silicates or aluminates yield much better characteristics, such as longer duration time of the phosphorescence, brighter luminosity and improved chemical stability, than the conventional sulphide materials used earlier [3–8].

Among the newly developed long afterglow materials, which have already found commercial use, akermanite structure based alkaline earth silicates $R_2MgSi_2O_7$ ($R = Ca, Sr, Ba$) codoped with Eu^{2+} and Dy^{3+} are of special interest because of their excellent persistent luminescence combined with an easy processability [9]. As in the case of Eu^{2+} and Dy^{3+} codoped MAI_2O_4 ($M = Ca$ and Sr), it is generally agreed that the long afterglow emissions arise from 5d–4f transitions of the Eu^{2+} ions following the thermal release of holes or electrons from the traps and subsequent transportation of the charge carriers or energy to the Eu^{2+} sites [10]. But the details about the nature of the different hole or electron traps and their roles in the processes involved in the persistent luminescence are still unclear. In the present work, the luminescence and the long afterglow from Eu^{2+} and Dy^{3+} codoped $Sr_{2-x}Ca_xMgSi_2O_7$ ($x = 0, 1$) was investigated under VUV–UV excitation from a synchrotron radiation source. In the light of these results, alongside with the data from laser-excited emission and thermoluminescence measurement, the nature of the traps responsible for the persistent luminescence of these two newly developed blue-emitting long afterglow phosphors will be discussed.

2. Experimental

The powder polycrystalline samples, $Sr_2MgSi_2O_7:Eu^{2+}$, Dy^{3+} (noted as SB-8C) and $SrCaMgSi_2O_7:Eu^{2+}$, Dy^{3+} (noted as SBG-8C), were prepared by solid state reaction method in reducing atmosphere ($N_2 + 5\% H_2$). $Sr(NO_3)_2$,

$CaCO_3$, MgO , SiO_2 , Eu_2O_3 , and Dy_2O_3 were used as raw materials, with 5 mol% excess of SiO_2 and 1 mol% H_3BO_3 as flux. The nominal concentrations of Eu^{2+} and Dy^{3+} are 0.5 and 8 mol%, respectively, for both samples. The mixture was ground to fine particles before sintering at $\sim 1300^\circ C$ for 3 h. The crystalline structure of the sample was verified at room temperature, by X-ray powder diffraction (XRD), using a D/max-rA diffractometer ($Cu K_\alpha$ radiation at $1.5406 \text{ \AA}$) over the range of $13\text{--}70^\circ$. The SB-8C sample is a white powder with long afterglow emission in blue after illumination by the normal visible light, e.g. sunlight or light from ordinary fluorescent lamps. The SBG-8C sample is a light-green powder with long afterglow emission in blue-green after illumination by the natural visible light. Both samples can show long afterglow with duration as long as 10 h. In our work, the powder samples were pressed into tablets with 10 mm diameter and ~ 0.5 mm thickness before spectroscopic measurements.

The luminescence and long afterglow emission spectra were measured at the SUPERLUMI station of HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron). The samples were mounted on the cold finger of a LHe flow type cryostat. The excitation spectra were corrected for the incident flux of the excitation beam using the excitation spectrum of sodium salicylate as a standard. The emission spectra were recorded using an Acton SpectraPro308i spectroscope coupled with a liquid nitrogen cooled CCD detector (Princeton Instruments Inc.). The emission spectra were not corrected for the sensitivity of the detection system. The long afterglow spectra were measured using the same set up, but with the beam shutter closed. The high-resolution laser-excited emission spectra of $Sr_2MgSi_2O_7:Eu^{2+}$, Dy^{3+} was measured at the Debye Institute of Utrecht University where an F_2 excimer laser was used as excitation source (157.6 nm).

A cryostatic sample chamber with multiple optical windows combined with a C-100S programmable temperature controller was used in the thermoluminescence glow curve measurements (250–450 K) for the integrated emission intensity.

The heating rate was 0.2 K/s. Monitoring the peak wavelength in the emission spectra, the thermoluminescence was also measured at the SUPER-LUMI set up using a CRYOVAC temperature controller in the temperature range of 40–320 K with a heating rate of 8 K/s.

3. Results and discussion

3.1. X-ray powder diffraction

Both $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{MgSi}_2\text{O}_7$ have an akermanite-type crystal structure which belongs to the tetragonal crystallography with space group $\text{P4}_2\text{m}$. $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7$ ($x = 1$) is a solid solution between $\text{Sr}_2\text{MgSi}_2\text{O}_7$ and $\text{Ca}_2\text{MgSi}_2\text{O}_7$, with same crystal structure as its constituents. The XRD patterns shown in Fig. 1 confirm the both samples obtained have an akermanite type structure with reasonable phase purity. A thorough comparison of the pattern (a) in Fig. 1 with those reported in Ref. [11] disclose some impurity phase indicated by “○”, which is coming from the SiO_2 inclusion due to the excess of SiO_2 was used in the preparation of the sample.

Fig. 1. XRD patterns for the sample $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (a) and the sample $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (b). In pattern curve (a), the peaks corresponding to $\text{Sr}_2\text{MgSi}_2\text{O}_7$ with akermanite structure are indicated with a “x”, and peaks coming from impurity phase are indicated with a “○”.

3.2. Luminescence under synchrotron radiation

The emission spectra of the SB-8C sample shown in Fig. 2 consist of two bands peaking at 477 and 578 nm when excited by 170 nm photons (curves a and b). The 477 nm broad band with full-width at half-maximum (FWHM) of 50 nm corresponds to the transition from the lowest crystal field components of the $4f^65d^1$ excited state configuration to the $^8\text{S}_{7/2}$ ($4f^7$) ground state of Eu^{2+} ions, which supposedly occupy the strontium sites in this akermanite structure host [12]. The 578 nm band arises from the intraconfigurational transition $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ ($4f^9$) of Dy^{3+} ions [13]. It should be noted that the transition from $^4\text{F}_{9/2}$ to the ground state $^6\text{H}_{15/2}$ of Dy^{3+} , located around 480 nm, is overlapping and thus obscured by the strong Eu^{2+} d–f emission, probably causing the asymmetry of 477 nm band. Under 300 nm excitation (curves c and d), the intensity of 578 nm decreases drastically (invisible in Fig. 2, but still observable in the enlarged scale), while the 477 nm band becomes more symmetrical. The emission at room temperature (RT) has the same behaviour as at low temperature, except for the much lower intensity due to a strong thermal quenching effect like in singly Eu^{2+} doped $\text{Sr}_2\text{MgSi}_2\text{O}_7$, in which the emission intensity at 300 K is only half of that at 4.2 K [12].

Fig. 2. Emission spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (SB-8C) under different excitation (170 and 300 nm) at 7.6 K and RT.

In the excitation spectra monitoring 477 nm emission from SB-8C sample (Fig. 3a), the dominating excitation band at wavelengths longer than 220 nm shows a complicated structure, comprising at least three sub-bands (around 250, 280 and 310 nm), which can be attributed to the transition from $^8S_{7/2}$ to the higher crystal field components of $4f^65d^1$ states of Eu^{2+} . The excitation band around 170 nm is assigned to the spin allowed f–d transition of Dy^{3+} , consistent with the results reported before [14,15]. The plateau structure in the short wavelength side of the 170 nm band indicates the interband transitions of the host material. From this, it can be assumed that the energy levels of the low-spin 5d states of Dy^{3+} are overlapping with the bottom of the conduction band. In the excitation spectra of the 578 nm emission (Fig. 3b), the long wavelength excitation bands beyond 300 nm are very weak, while the 170 nm band and some structures in the range of 180–200 nm are dominating excitation bands. The origin of the excitation in the range of 180–200 nm is not very clear. But from the nearly absence of excitation band corresponding to the interband transitions in the shorter wavelength range (<170 nm) and the f–d transitions of Eu^{2+} ions in the longer wavelength range (>220 nm) in the excitation spectra of 578 nm emission, it is

reasonable to conclude that the excitation of the Dy^{3+} 4f–4f luminescence are mainly through the Dy^{3+} -related absorption. The comparison of the two excitation curves indicates that the absorbed energy at Dy^{3+} sites can be efficiently transferred to the Eu^{2+} ions, possibly involving the conduction band, while back transfer of the energy from Eu^{2+} to Dy^{3+} or from the host to Dy^{3+} is not very significant.

The emission of the SBG-8C sample is similar to that of the SB-8C, except that the peak position of the 5d $\rightarrow$ 4f emission from Eu^{2+} shifts from 477 nm (blue) in SB-8C to 491 nm (blue–green) in SBG-8C and the $^4F_{9/2} \rightarrow ^6H_{13/2, 15/2}$ emission from Dy^{3+} has a higher proportion in the total emission in the case of SBG-8C than in the case of SB-8C. These differences are pronounced in the comparison between the emission spectra of the two samples shown in Fig. 4. The high resolution of the spectra in Fig. 4 is due to the smallest slit width (0.01 mm) that can be used in the measurements. Benefiting from this high resolution, two groups of emission lines were resolved: the 478, 483 and 493 nm lines corresponding to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ transitions of Dy^{3+} ions, which overlap with the broad 5d $\rightarrow$ 4f emission band of Eu^{2+} ions; and the 574, 576, 579, 581 and 585 nm lines corresponding to the $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy^{3+} ions. It is not

Fig. 3. Excitation spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (SB-8C) monitoring different emissions (477 and 578 nm) at 11 K.

Fig. 4. Emission spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (SB-8C) and $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (SBG-8C) under 170 nm excitation at 9 K.

surprising that the relative intensities of respective lines are different in the two emission spectra because of different local environments of Dy^{3+} ions, which are supposed to occupy the Sr or Ca sites in the hosts.

Fig. 5 shows the excitation spectra of SBG-8C monitoring 491 and 578 nm emissions at 11 K. The excitation spectra of the 491 nm emission are rather similar to the excitation spectra of the 477 nm emission of SB-8C shown in Fig. 3. This means the same excitation mechanism accounts for the Eu^{2+} 5d $\rightarrow$ 4f emission in the two different hosts. The major difference caused by the presence of calcium in the host of SBG-8C is the increased intensity of the excitation band around 120 nm. This observation supports the conclusion that the shorter wavelength excitation below 170 nm is corresponding to interband transitions of the hosts. The excitation spectra of 578 nm emission of SBG-8C is dominated by the 170 nm excitation band corresponding to the spin-allowed transition from ground state $^6\text{H}_{15/2}$ to the lowest low-spin 5d levels of Dy^{3+} ions. The excitation band around 193 nm corresponding to the transitions from ground state $^6\text{H}_{15/2}$ to the high-spin 5d levels of Dy^{3+} ions is extremely weak in comparison with the dominating 170 nm band. The difference between the excitation spectra of the two samples

suggests that the energy transfer from the low-spin 5d levels of Dy^{3+} to the 5d levels of Eu^{2+} , probably via the conduction band, is more efficient in SB-8C. This causes the intensity loss of 170 nm excitation band in the spectra of SB-8C monitoring the Dy^{3+} 4f–4f luminescence (Fig. 3, curve b).

The structure of akermanite host can be characterized by tetrahedral sheets consisting of $[\text{Si}_2\text{O}_7]$ dimers interconnected by tetrahedrally coordinated Mg cations in the form of five-membered rings [16]. These sheets lie parallel to the (001) plane and are linked together along the c axis by large Sr or Ca cations in distorted eight-coordinated site. The alkaline earth ions form chains along the c axis. The doping rare earth ions, Eu^{2+} or Dy^{3+} , will occupy some of Sr or Ca sites in these chains. According to Poort et al. [12,17,18], a divalent europium ion in these chains experiences positive charges due to cation neighbours in the chain direction, in addition to the negative charges of the nearest anion neighbours. The positive charges can orient one 5d orbital of Eu^{2+} preferentially, thus lowering its energy and resulting in Eu^{2+} 5d $\rightarrow$ 4f emission at long wavelengths. In the case of $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7$, because of the fact that the distance between the alkaline earth ions along the c axis increases in going from calcium to strontium, the orientation of a d orbital will energetically become less favorable in this sequence. This implies that the emission is expected to shift to higher energy (shorter wavelength). This model supplies a good explanation for the fact that the peak position of the 5d $\rightarrow$ 4f emission band of Eu^{2+} shifts from 491 nm in SBG-8C to 477 nm in SB-8C. On the other hand, the presence of calcium in the alkaline earth chain seems to prevent the efficient energy migration along the c axis, especially energy transfer from low-spin 5d levels of Dy^{3+} to the excited states of Eu^{2+} , thus reserving a high proportion of Dy^{3+} luminescence in the total emission of SBG-8C.

3.3. Afterglow spectra under 170 nm irradiation

Fig. 6 presents the long afterglow emission spectra of SB-8C measured at different tempera-

Fig. 5. Excitation spectra of $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (SBG-8C) monitoring different emissions (491 and 578 nm) at 11 K.

Fig. 6. Long afterglow of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ under 170 nm irradiation at different temperatures (the measurements started ~ 30 s after closing the beam-shutter at each temperature).

tures after irradiation at 170 nm. The long afterglow emission spectra consists of a band around 477 nm similar to that observed in emission spectra by 300 nm excitation (Fig. 2, curves *c* and *d*). This indicates that the long afterglow emission is due to the d–f transitions of Eu^{2+} ions, as in other Eu^{2+} doped silicate or aluminate long afterglow phosphors. The long afterglow emission exists only at temperature higher than 200 K, and its intensity increases with rising temperature, at least up to 280 K. The results about the long afterglow of SBG-8C are similar to those of SB-8C except the red shift of the peak position of the emission band. These results were expected because the long afterglow emission can be understood as a special kind of thermoluminescence, with thermal release of the carriers from traps of suitable depth occurring at room temperature efficiently and continuously.

3.4. Emission spectra under 157.6 nm laser excitation

Before looking at the thermoluminescence curves, which disclose more information concerning the traps, it would be useful to introduce here the high-resolution emission spectra of SB-8C excited by 157.6 nm laser at room temperature (see Fig. 7). The laser-induced luminescence shows some different features compared to the emission spectra measured with synchrotron radiation excitation. This does not originate from the different excitation wavelength. We repeated the emission spectra with 157 nm synchrotron radiation excitation. They were very similar to those excited with 170 nm. The spectral differences between Fig. 7 and Fig. 4 are ascribed to the high excitation density of the laser source, which is many orders of magnitude higher than the excitation density achieved with synchrotron radiation.

The most obvious new features in the laser-excited emission spectra are three groups of sharp emission lines centred around 590, 614 and 626 nm, which are known red emissions of trivalent europium corresponding to intraconfigurational 4f–4f transitions: $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (614 and 626 nm). The presence of Eu^{3+} emissions, which are not observed under synchrotron radiation excitation, indicates an efficient photon-induced process, which promotes

Fig. 7. Emission spectra of $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ excited by 157.6 nm laser at room temperature.

Eu^{2+} to Eu^{3+} under high-intensity laser excitation. As a result of this laser-induced process, the contribution from the Eu^{2+} $5d \rightarrow 4f$ emissions in the total luminescence diminishes substantially, almost obscured by the stronger ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ emission of Dy^{3+} located in the same range (470–490 nm).

The high efficiency of Eu^{2+} – Eu^{3+} conversion by laser means a high ionizability of the Eu^{2+} ions in the host. In turn, this high ionizability of the Eu^{2+} ions perhaps implies either an involvement of Eu^{2+} ions in hole trap formation, or the hole traps in the vicinity of the Eu^{2+} ions, thus the energy barrier for the ionization of Eu^{2+} is lowered. Because we did not observe the $4f$ – $4f$ emissions from Eu^{3+} under synchrotron radiation, the possibility of Eu^{2+} ions acting directly as hole traps to form Eu^{3+} can be neglected. On the other hand, various lattice defects, which are abundant in the host were suggested to play important roles in the trap formation. For example, alkaline earth ion vacancy, V_{M} , which is introduced in the host through charge compensation effect as a result of trivalent Dy ions on the divalent Sr sites, is a plausible hole trap. Taking consideration of the much higher concentration of Dy^{3+} in the host (8 mol%) compared with the low concentration of Eu^{2+} (0.5 mol%), it is reasonable to believe that there must be hole traps formed by V_{M} close to Eu^{2+} ion. In the process of laser excitation, the initial photon ionizes Eu^{2+} to form Eu^{3+} via displacement of hole from V_{M} to the Eu site, and the second photon lifts the Eu^{3+} to its excited states. Consequently, the $4f$ – $4f$ emissions from Eu^{3+} are achieved upon the high-density laser excitation.

3.5. Thermoluminescence

In the thermoluminescence curves monitoring the integrated emission intensity in the visible range (see Fig. 8(a)), the peaks of thermoluminescence are at 358 and 328 K for SB-8C and SBG-8C, respectively. For the thermoluminescence monitoring the $5d \rightarrow 4f$ emission of Eu^{2+} (Fig. 8(b), curves *a* and *b*), the peak positions are shifted to 304 and 285 K, respectively. The thermoluminescence intensities monitoring ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ emis-

sions of Dy^{3+} (Fig. 8(b), curves *c* and *d*) are about two magnitudes weaker than that monitoring Eu^{2+} emission. This is consistent with the fact that the long afterglow is mainly due to the emission at Eu^{2+} sites. Though in Fig. 8(b) we cannot determine the peak position of the rising bands in the thermoluminescence curves *c* and *d* above 270 K because of temperature limitation of the sample holder in the current measurements, the weak peaks at 147 and 145 K are clearly resolved in curves *c* and *d*, respectively, which indicate a small amount of shallow traps associated with Dy^{3+} only. The much stronger and broader glow emission bands in Fig. 8(a) and also in curves *a* and *b* of Fig. 8(b) imply a complicated nature of traps involved in the long afterglow emission. The precise determination of the trap depth can be done only with help of preheating method or peak shape method, but a comparison of Fig. 8(a) with the thermoluminescence peaks of $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ in the similar range measured with the same heating rate (0.2 K/s) [19] gives a rough estimation of the trap depth of 1.2 and 1.0 eV for SB-8C and SBG-8C, respectively.

3.6. Long afterglow mechanism

In the previous studies on Eu^{2+} and Dy^{3+} codoped long afterglow phosphors, Eu^{2+} was proposed to act as electron traps to form Eu^+ , while Dy^{3+} was proposed to act as hole traps to form Dy^{4+} [20–22]. But the stabilization of Eu^+ and Dy^{4+} is energetically dubious. As an alternative, various defect-related centres, such as alkaline earth cation vacancies V_{M} and oxygen vacancies V_{O} , were suggested to play important roles in the trap formations [10]. From the preceding discussions of the laser excited luminescence, it can be concluded that V_{M} is a very probable candidate for hole trap, and that the efficient Eu^{2+} – Eu^{3+} conversion under the laser excitation can be attributed to the hole traps formed by V_{M} in the vicinity of the Eu^{2+} ions.

These hole traps formed by V_{M} defects have a long lifetime at room temperature. The broad thermoluminescence around and above room temperature is largely due to the release of the holes trapped at V_{M} defects. Then the energy

Fig. 8. Thermoluminescence curve of $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ (a) monitoring the integrated emission intensity after irradiation under low-pressure mercury lamp with heating rate 0.2 K/s; (b) monitoring the spectrally resolved emission after irradiation under 170 nm synchrotron radiation with heating rate 8 K/s. The sample name and the monitored wavelength (λ_{em}) are specified in the legend.

released by the electron–hole recombinations transfer to Eu^{2+} ions (perhaps via cross relaxation), exciting Eu^{2+} to 5d states, and finally yielding the emission from 5d $\rightarrow$ 4f transitions of the Eu^{2+} ions. The longer the distance between the alkaline earth vacancy and the nearest alkaline earth ions, the higher the energy needed for the release of the holes to the valence band, therefore

the fact that the traps are deeper in SB-8C (1.2 eV) than in SBG-8C (1.0 eV).

4. Conclusion

The luminescence studies of long afterglow phosphors $\text{Sr}_{2-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ ($x=0, 1$)

were reported along with the phenomenological discussion concerning the traps responsible for the persistent luminescence. The possibility of V_M acting as hole traps was proposed as well as the correlation between the trap depth and the distance between the V_M defects and the nearest alkaline earth ions. However, for the detailed information about the traps as well as the dynamics involved in the long afterglow process, further investigations are needed.

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