



## TiO<sub>2</sub>:Sm<sup>3+</sup> based luminescent oxygen sensitive probes in LDPE packaging material

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**Abstract.** In present work it was attempted to prepare luminescent TiO<sub>2</sub>:Sm<sup>3+</sup> microprobes embedded into low density polyethylene (LDPE) films for real-time non-intrusive detection of oxygen contamination in plastic film of food packages with a long term goal of streamlining the quality control mechanisms in food packaging process. The luminescence of TiO<sub>2</sub>:Sm<sup>3+</sup> has previously been reported to be a usable for optical sensing of O<sub>2</sub> and other gases [1]. In current work we also show that its thermal stability makes it especially suitable for thermo polymer industry as it can withstand required thermal treatments encountered in different polymer processing stages without losing its ability to function as an O<sub>2</sub> probe. Sol-gel-prepared TiO<sub>2</sub>:Sm<sup>3+</sup> microparticles were embedded into LDPE by direct mixing [2] and hot pressing the polymer in molten state. The optical response of the doped films to various O<sub>2</sub> ambient concentrations are reported in comparison to pristine TiO<sub>2</sub>:Sm<sup>3+</sup> powder. The shortcomings in the sensor performance due to poor oxide particle size control must be paid attention in the future.

**Key words:** TiO<sub>2</sub>, Sm<sup>3+</sup>, oxygen sensor, extrusion, LDPE.

### 1. INTRODUCTION

Food safety and quality control during the process of packaging and delivery to the customer are one of the most essential parts of the food manufacturing process. In order to extend the useful lifetime of the food product, most of them are sealed into packages with modified atmosphere, usually consisting of 100% N<sub>2</sub> or mixture of N<sub>2</sub> and CO<sub>2</sub>. The concentration of oxygen as the most reactive component of ambient atmosphere is usually lowered down to 2–0.5% to prevent food spoilage. Excess oxygen can lead to fast, premature oxidative changes (e.g. discoloration of meat or fruits)

and accelerated microbial activity within the package and therefore shorten the lifetime of the product.

Oxygen can get into the package in different ways. The packed product itself may contain excessive oxygen that can spoil the food inside the package or oxygen can diffuse out from it and affect other parts of the package. Oxygen can also leak in through the plastic package material. The oxygen permeation rate through the packaging material has to be lowered to acceptable level for every specific food product by using additives or multilayer lamination approach. It is also important to ensure that the material would not have micro holes.

The third and the most common source of oxygen contamination comes from the sealing of the package. The latter is usually done by brief hot melting two

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sheets of packaging material together to form a gastight seal [3,4].

In order to ensure quality the sealing process should be continuously monitored for fault detection as even a small imperfection can lead to premature contamination.

Currently faulty packages are discovered by human visual estimation and random selection of packages is tested for quality, destructively. A real-time in-situ monitoring of packages' internal atmosphere could vastly improve the fault detection.

In current work we investigate the possibility of incorporating inorganic, oxide based sensory nanoparticles into low density polyethylene films as in-situ luminescent sensors for quality control of the oxygen contamination in packages after sealing. We use sol-gel prepared  $\text{Sm}^{3+}$  doped  $\text{TiO}_2$  powder as an oxygen probe embedded in LDPE film to demonstrate its usability in potential industrial setup for food packaging industry.

The incentive to use an inorganic additive as opposed to already well known oxygen photoluminescence quenching sensors based on different Pt or Ru complexes, stems from the fact that the latter needs to be incorporated inside the package separately, usually as a separate glued film because of intolerance to extrusion temperatures, which are experienced by the packaging material itself during manufacturing ( $\sim 190\text{--}230\text{ }^\circ\text{C}$  of LDPE [5]).  $\text{TiO}_2$  on the other hand can withstand such temperature easily (melting point is dependent on purity of  $\text{TiO}_2$   $\sim 1850\text{--}1870\text{ }^\circ\text{C}$  [6,7]). Secondly,  $\text{TiO}_2\text{:Sm}^{3+}$  is already well known as an optical gas probe.  $\text{O}_2$  sensing with  $\text{TiO}_2\text{:Sm}^{3+}$  was described first by Reedo et al. already in 2005 [8]. The long lifetime of the  $\text{Sm}^{3+}$  ions' photoluminescence (PL) of up to  $\sim 1$  ms and its unique spectral shape is particularly well suited for applications where identification of signal in noisy environment is needed.

## 2. EXPERIMENT

The aim of the experimental work was to prepare pure  $\text{TiO}_2\text{:Sm}^{3+}$  micro particles, mix them with LDPE and prepare film samples from the former in order to carry out comparative optical  $\text{O}_2$  sensing measurements in controlled ambient environments.

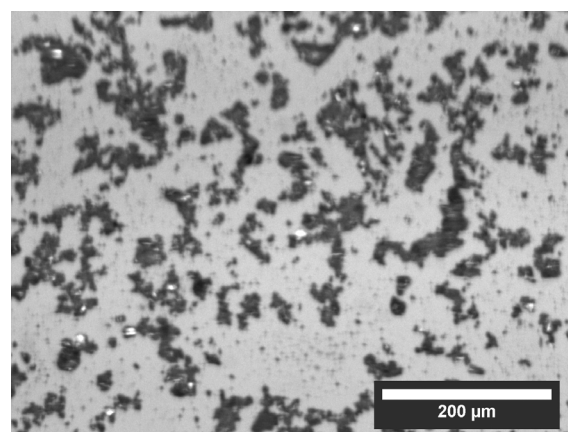
$\text{TiO}_2\text{:Sm}^{3+}$  particles were prepared via sol-gel route by adding  $\text{SmCl}_3$  and  $\text{Ti}(\text{O}i\text{Bu})_4$  in 1:1 molar ratio. 1 wt% of  $\text{SmCl}_3$  was dissolved in water.  $\text{Ti}(\text{O}i\text{Bu})_4$  was diluted in butanol. The former was then mixed into the  $\text{Ti}(\text{O}i\text{Bu})_4$  solution in small amounts and stirred constantly to avoid premature gelation of the solution. Butanol was extracted from the mixture by vacuum evaporation at  $70\text{ }^\circ\text{C}$  until dry. Final gelation took place by pumping humid air into the reaction vessel for a day.

The retrieved material was then annealed up to  $800\text{ }^\circ\text{C}$  for 1 h to ensure formation of crystalline material.

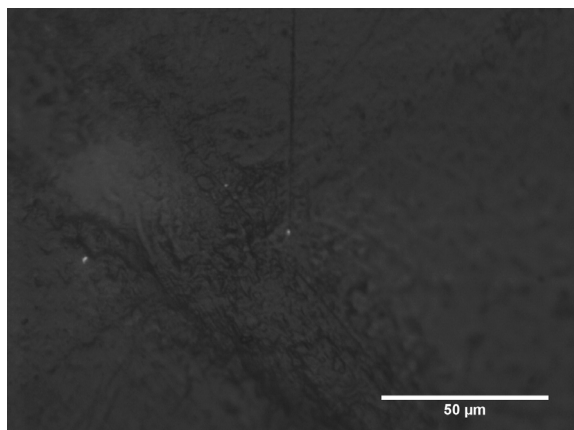
The material was manually crushed into microparticles in the mortar with bead mill (using zirconium oxide ceramic beads). Optical microscopy showed that the particles of both samples had very similar largely non-uniform size distribution. There was large amount of fairly large particles with diameter of up to  $\sim 50$  microns (see Fig. 1).

To imitate the end use in a packaging material, the oxide powder was dispersed in LDPE at 1 wt% and 10 wt% concentrations by twin-screw compounding method. As a proof of concept the polymer film samples were prepared by hot-pressing technique that resembles to a certain degree hot-melt processing techniques like blown film extrusion and cast film extrusion, used in the packaging industry. The prepared samples were made  $\sim 200\text{ }\mu\text{m}$  thick, which is close to the upper limit for applications in regular food packaging but enables us to observe diffusion properties of  $\text{O}_2$  in LDPE in a longer time scale. The dispersion of the oxide particles within the polymer film was good with only very few bigger agglomerates (see Fig. 2). In general, good dispersion is desired in gas sensor design as it increases the surface to volume ratio of the probe.

Photoluminescence (PL) spectra measurements were carried out for both samples using a pulsed Nd:YAG laser using a 355 nm laser for excitation. General spectroscopic characterization was conducted in ambient air. For assessing gas sensing performance the samples were placed into a flow-through type of optical cell (Linkam Inc.). The PL spectra intensity of the samples was continuously registered throughout a series of gas mixtures consisting of periods of pure  $\text{N}_2$  and  $\text{N}_2 + \text{O}_2$  mixtures with  $\text{O}_2$  partial pressures in the range from 10 to 100%. Chosen oxygen concentrations exceeded that



**Fig. 1.** Micrograph of pristine  $\text{TiO}_2\text{:Sm}^{3+}$  particles after mechanical crushing in bead mill with zirconia medium.

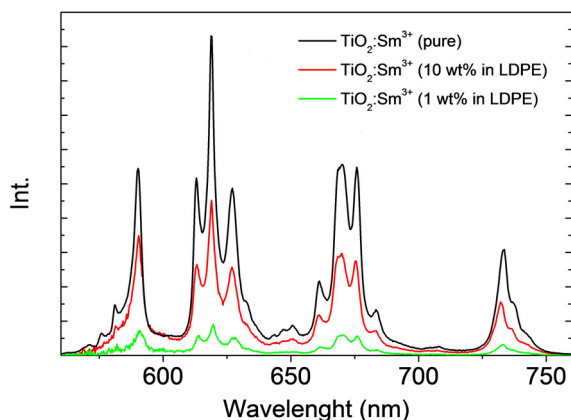


**Fig. 2.** Optical micrograph of  $\text{TiO}_2\text{:Sm}^{3+}$  micro-particles in LDPE film.

of the typical food packaging applications but displayed more manageable differences in sensitivity that were difficult to register at lower concentrations due to decreased signal to noise ratio. Prior to each gas sensing measurement the samples were heated in pure nitrogen and 5%  $\text{O}_2$  mixture for 10 minutes at  $100^\circ\text{C}$  to ensure water vapour removal which could affect measurements.

### 3. RESULTS AND DISCUSSION

PL spectra of prepared  $\text{TiO}_2\text{:Sm}^{3+}$  particles in ambient air and under optical 355 nm laser excitation revealed characteristic  $\text{Sm}^{3+}$  ion's 4f shell line spectra reported also by numerous other authors (see Fig. 3) [9,10]. In nominally pure  $\text{TiO}_2$ , defect related intrinsic PL is usually present at  $\sim 500\text{ nm}$  as a wide band [11]. In current case this intrinsic defect related emission was



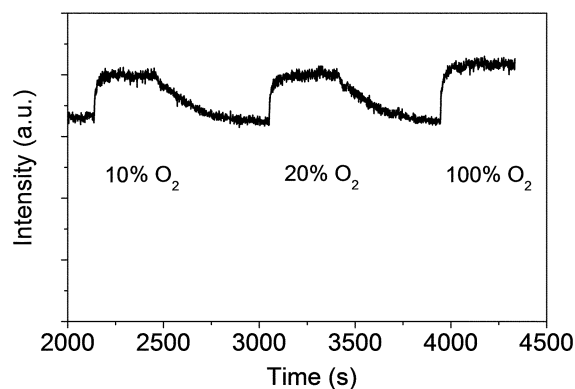
**Fig. 3.** PL emission spectra of  $\text{TiO}_2\text{:Sm}^{3+}$  as oxide powder and while embedded in LDPE film.

not present or was too weak to be comparable to the dopant PL. The PL spectra remained largely unaffected when embedded in LDPE thin film samples (see Fig. 3). The intensity of the PL spectra expectedly increased as  $\text{TiO}_2$  concentration in polymer was raised.

The PL of  $\text{TiO}_2\text{:Sm}^{3+}$  powder was found to be only moderately sensitive to the changes in ambient  $\text{O}_2$  partial pressure as shown in Fig. 4. Because of the latter and the fact that in case of the LDPE film samples, the PL intensity was also modulated by long term drift due to  $\text{O}_2$  outgassing from the polymer matrix, we from here on characterize changes in the sensor output with PL response, defined as the relative PL intensity change:  $S = (I - I_0)/I_0$ . Here  $I_0$  indicates PL intensity at base level with zero percent  $\text{O}_2$  in  $\text{N}_2$  and  $I$  indicates PL intensity at probed percentage of  $\text{O}_2$  in  $\text{N}_2$ . For all measurements the baseline intensity corresponding to 0% oxygen was determined by a polynomial fit and used as a reference for  $I_0$  in sensitivity calculation.

For defining adequate parameters for characterizing the response speed, the temporal nature of the gas response should be considered. In current case we found that single exponential in the form  $S = S_0 + Ae^{-t/\tau}$  fits well with the increasing PL signal (during  $\text{O}_2$  exposure) of all tested samples. Hence, we can characterize the response speed to a particular  $\text{O}_2$  concentration with a single time constant  $\tau$ . The results for all fittings with maximum response values reached during oxygen exposures are presented in Table 1.

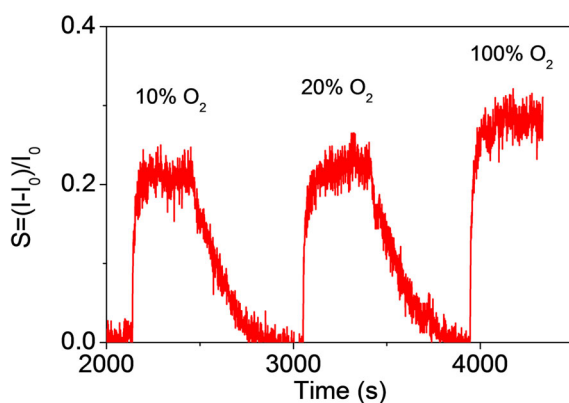
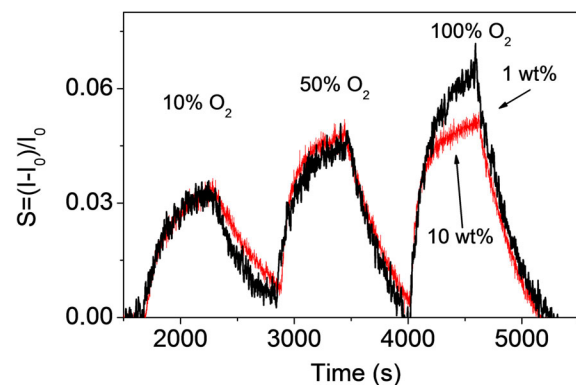
By examining the sensitivity curves of  $\text{TiO}_2\text{:Sm}^{3+}$  powder (see Fig. 5, Table 1) it can be concluded that it has rather modest maximum sensitivity in the range from 0.2–0.3 and a fast average response speed of  $\tau \sim 30\text{ s}$ . The sensitivity shows rather small reduction in the series indicating that prepared material could be used at levels of  $\text{O}_2$  much lower than currently used minimum of 10%.



**Fig. 4.** PL intensity changes of  $\text{TiO}_2\text{:Sm}^{3+}$  powder at different ambient  $\text{O}_2$  concentrations in  $\text{N}_2$  background.

**Table 1.** Maximum sensitivity values and corresponding time parameters for all measured samples at given oxygen concentrations

O <sub>2</sub> concentration %	TiO <sub>2</sub> :Sm <sup>3+</sup> powder		10 wt% TiO <sub>2</sub> :Sm <sup>3+</sup> in LDPE		1 wt% TiO <sub>2</sub> :Sm <sup>3+</sup> in LDPE	
	$S_{\max}$	$\tau$ , s	$S_{\max}$	$\tau$ , s	$S_{\max}$	$\tau$ , s
10	0.2	22	0.033	178	0.035	197
20	0.22	31	–	–	–	–
50	–	–	0.048	141	0.045	187
100	0.28	30	0.05	–	0.06	138

**Fig. 5.** Response of  $\text{TiO}_2\text{:Sm}^{3+}$  powder at different ambient O<sub>2</sub> concentrations.**Fig. 6.** Response of LDPE embedded  $\text{TiO}_2\text{:Sm}^{3+}$  samples at different doping concentrations.

Poor sensitivity in current case is most probably related to the low surface-to-volume ratio of the micro-particles leaving large part of optically active emitting  $\text{Sm}^{3+}$  ions too far from the surface and unaffected by exposure to O<sub>2</sub>.

The recovery time is noticeably longer than initial response to O<sub>2</sub> indicating that desorption of O<sub>2</sub> molecules from TiO<sub>2</sub> surface most probably possesses different energetic barrier to adsorption.

When the sensor particles are embedded in LDPE film, reduction of maximum sensitivities on average of about 5–6 times can be seen (Fig. 6, Table 1). The response speed is prolonged also by more than 5 times. Remarkably the curves are rather similar for both doping levels with the only exception being 10 wt% sample when exposed to 100% O<sub>2</sub>.

We can propose that if all probe particles are spread out evenly throughout the film thickness then temporal response should indeed not depend on their concentration as all probe particles are simultaneously optically excited and gas diffusion is controlled solely by the permeability of the LDPE film with no interference from additives. The kinetics could be said to be diffusion limited only.

If this is mainly the case, then at 10 wt% with 100% O<sub>2</sub> exposure, most probably high amount of TiO<sub>2</sub> particles can cause a deviation from the presumption. The contribution and variability of this effect needs to be assessed further at industrially relevant probe concentrations within the polymer film in further stages of the work.

#### 4. CONCLUSIONS

Current investigation revealed that  $\text{TiO}_2\text{:Sm}^{3+}$  based luminescent oxygen probe particles can withstand the thermal processing of industrial melt-extrusion process used in packaging industry. The gas response performance of  $\text{TiO}_2\text{:Sm}^{3+}$  in currently prepared form is limited due to large particle size, which leads to poor surface-to-volume ratio. Nevertheless the consistent response within the tested range from 10% to 100% O<sub>2</sub> indicated that the material has potential for detecting also much lower concentrations especially if the preparation methods could be refined to produce smaller particle sizes. The response time of the LDPE embedded  $\text{TiO}_2\text{:Sm}^{3+}$  particles was acceptable, with characteristic time constants in the range from ~130–200 s at tested O<sub>2</sub> concentrations.

Independence of the sensitivity and its speed from additive concentration in LDPE suggests that very low additive amount could be used in industrial applications. Further refinements to the methods of oxide particle preparation shall be made in the future to reduce their size to gain sensitivity.

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### TiO<sub>2</sub>:Sm<sup>3+</sup> baseeruvad luminesceeruvad hapniku sensorid LDPE pakkematerjalides

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Käesoleva uurimistöö eesmärgiks oli valmistada TiO<sub>2</sub>:Sm<sup>3+</sup> baseeruv mikroskaalas sensormaterjal ja dispergeerida see madaltihedast polüetüleenist (LDPE) kilesse, et tekitada toiduainepakendites reaajas jälgitav ning mitte-destruktiivne hapniku kontsentratsiooni jälgimise viis pikaajalise eesmärgiga hõlbustada toidu pakendamisprotsessis kvaliteedikontrolli.

TiO<sub>2</sub>:Sm<sup>3+</sup> luminescentsomadusi on eelnevalt hapniku ja ka teiste gaaside detekteerimiseks edukalt kasutatud. Käesolevas töös on näidatud, et lisaks sellele on antud materjalil ka hea termiline stabiilsus, mille tõttu sobib see suurepäraselt termoplastide tööstusesse, kus peale mehaanilise vastupidavuse peab sensormaterjal peale termilist töötlemist säilitama ka oma tundlikkuse hapniku suhtes.

Sool-geel-meetodil valmistatud TiO<sub>2</sub>:Sm<sup>3+</sup> mikroosakesed dispergeeriti LDPE maatriksisse otsese mehaanilise segamise teel [2] ja vormiti katsekehadeks kuumpressimise meetodil. Dopeeritud kile optiline signaal erinevatele ümbritseva atmosfääri O<sub>2</sub> kontsentratsioonidele on välja toodud võrrelduna puhta TiO<sub>2</sub>:Sm<sup>3+</sup> pulbri signaaliga. Puudujäägid sensori toimimises, mis tulenevad peamiselt oksiidiosakeste suuruse heterogeensusest, tuleb edaspidi tähelepanu alla võtta.