



Review

Photoluminescent porous and layered lanthanide silicates: A review



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ABSTRACT

A large number of silicates containing transition metals and rare earth (in particular lanthanide) elements have been reported until recently. Generally, they exhibit a rich structural chemistry with interesting physical and chemical properties, and, in contrast to zeolites, which are built of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedrons, their frameworks embody metals in different coordination. In particular, materials containing rare earth and/or lanthanide elements may combine, in a single and stable solid, microporosity and tuneable optical properties. Such multi-functionality may be explored with interest, being a challenging approach to novel chemical and optical applications.

This article aims to review rare earth and lanthanide silicates published to date, namely their relevant structure features and photoluminescent properties, being divided in two sections according to the major approaches used for their preparation, *i.e.* doping and embedding. The parent materials hosting the rare earth or lanthanide elements, the type and number of such emitters, and the disorder and dimensionality of the solids are some of the addressed topics. Furthermore, this review is also intended to highlight the great challenges that optical centres design offers in the field of material science. Some potential applications are also debated, such as wastewater remediation, nuclear medicine, imaging, and sensors. Notwithstanding the relevance that photoluminescent porous and layered lanthanide silicates may achieve in wastewater treatment, as a result of their stability and high selectivity combined with capacity, their sensing ability towards a specific ion or molecule will be of capital importance in the near future.

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1. Introduction

Zeolites and zeolitic materials, like aluminophosphates (AlPOs), silicoaluminophosphates (SAPOs) and metalaluminophosphates (MeAPOs), have crystalline open-framework structures assembled from tetrahedral units interconnected to each other by sharing all

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the oxygen atoms to form intracrystalline hollow spaces and channels of molecular dimensions. Zeolites are aluminosilicates built of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, and the negative charge of the framework is balanced by a range of extra-framework cations, which render them ion exchange properties. When the $[\text{SiO}_4]^{4-}$ is substituted by $[\text{PO}_4]^{3-}$ tetrahedra, aluminophosphates known as AIPOs are originated. Furthermore, the addition of another element to the aluminophosphate frameworks, for example, Si, metal ions Mg, Co, Mn, Fe, as well as others, led to the silicoaluminophosphate and metalloaluminophosphate families, SAPO and MeAPO, respectively. AIPO frameworks have no net charge and so they possess little catalytic potential and no cation exchange ability [1]. Although the briefly described structures of the previous zeolites and zeolitic materials are all based on tetrahedral building units, some others microporous structures like manganese oxides with entirely octahedral framework atoms have also been reported [2].

The main aspect to retain in this context is the possibility of constructing materials based on heteropolyhedras, such as octahedra, pentahedra and tetrahedra (OPT). The OPT materials [3,4] are not simply an interesting addition of zeotype solids, since they have been investigated for over 25 years and already include more than one hundred different entities with new properties. In the last decade, much research was developed on the syntheses of materials comprising transition metals and rare earth (RE) (especially lanthanides, Ln) guests in mixed OPT microporous silicates hosts. The latter one is attracting much interest due to their optical properties and was reviewed in 2003 by Rocha and Carlos [5], in 2005 by Rocha and Lin [6] and in 2013 by Rocha et al. [7]. The preparation of zeotype Ln-silicates is an emerging field since the beginning of this century, though they are being essentially investigated as phosphor materials and as probes to obtain information about the structure and environment inside the cages where cations are located [8,9]. Nevertheless, they can combine, in a single and stable crystalline structure, microporosity and tuneable optical properties, which makes them interesting materials for potential applications in many devices, for example in cathode ray tubes, projection televisions, fluorescent tubes and X-ray detectors, and in photonics and optical communications [10]. Moreover, recently, considerable attention has been given to them since they can play an important role in the field of wastewater remediation as inorganic exchangers with sensing ability to cations [11–13].

The lanthanide series comprises fifteen chemical elements with atomic numbers 57 through 71, from lanthanum to lutetium. The fifteen lanthanides, along with chemically similar scandium and yttrium, are often collectively known as rare earth elements, and all of them form (at least) trivalent cations, hereafter denoted by Ln^{3+} . Materials that contain lanthanide elements can emit over the entire spectral range: near infrared (Nd^{3+} , Er^{3+}), red (Eu^{3+} , Pr^{3+} , Sm^{3+}), green (Er^{3+} , Tb^{3+}), and blue (Tm^{3+} , Ce^{3+}) [14]. Their optical transitions occur only between 4f orbitals, which are well shielded from their chemical environment by $5s^2$ and $5p^6$ electrons and, as a consequence, atomic-like emission spectra displaying characteristic sharp lines may be observed [5]. However, the emission spectrum of a given material may be influenced by the presence of neighbouring molecules and/or ions, and thus the possibility to sense their presence in the matrix may be explored with interest. The change of photoluminescence response induced by ions sorption has been recently investigated for sensing purposes [11–13], while the entrapment of molecular species in zeolitic cavities acting as luminescence centres or activators of the framework Ln^{3+} ions has not been yet pursued.

To introduce lanthanide ion centres into microporous silicates there are at least two possible ways [5,6]. One way is to ion exchange the Na^+ and K^+ located inside the pores of the pre-synthesized material by Ln^{3+} cations. Another way is to embed

the Ln^{3+} cations in the microporous framework, resulting in silicates that contain stoichiometric amounts of these elements. This approach was described in detail firstly by Rocha and Carlos [5] in 2003. There are also two other feasible ways of hosting lanthanide luminescent centres in microporous materials, namely, by enclosing lanthanide complexes with organic ligands in zeolitic open spaces and coordinating organic species to metal frameworks (Porous Coordination Polymers – PCPs – and Metal-Organic Frameworks – MOFs) [15,16]. This review will focus on inorganic materials, especially metal and lanthanide silicates, and therefore those two other approaches will not be discussed here.

The aim of this article is to review the structure and associated photoluminescent properties of lanthanide materials. The principal structures of Ln-silicates reviewed in this paper are resumed in Table 1, which contains their general formulas and, when possible, their names and mineral analogues. It is also indicated how many RE/Ln sites the structure possesses, since it is an important feature for these classes of materials.

The review is divided as follows: The general introduction (Section 1) that finishes with the relevance of the article (Section 1.1); The main contents of the review are presented and discussed in Section 2, namely: *Materials doped with lanthanides via ion exchange* (post-synthesis; Section 2.1), and *Lanthanide silicates* (Section 2.2). The last one is split into *microporous* (Section 2.2.1) and *layered* (Section 2.2.2) lanthanide silicates.

The zeolitic materials were included in Section 2.1 since they play a chief role in catalysis. In fact, most of these family members have a significant position in several applications where the light emission is one of the less explored. Moreover, it is important to realize that if it is feasible to incorporate lanthanides as part of extra-framework cations in a structure, these light-emitting ions may turn possible to understand the distribution and coordination of other ions/molecules in aluminosilicates. An example that confirms the relevance of zeolites as light emitters is the case of zeolite NaY, a microporous aluminosilicate that has hydrated Ln^{3+} ions in its large cavities; more specifically, Gadolite, a Gd^{3+} modified zeolite NaY that possesses great potential as magnetic resonance imaging contrast agents [17].

The lanthanide silicates are divided into microporous and layered solids. The main purpose of focusing such layered materials separately is to show that they gave an important contribution to the study of the evolution of photoluminescence across Ln-containing silicates dimensionality [18,19]. In other words, it is intended to explain that by changing the structural dimensionality of lanthanide (or transition metal) materials it is possible to tune their light-emission properties. Hence, if it is of interest to use them as sensors and other devices, layered lanthanide silicate nanoparticles may also be explored.

1.1. Relevance of the review

Since RE/Ln-silicates combine in a single and stable solid microporosity and tuneable optical properties, it is important to keep seeking for applications where optical features may be of interest. In this context, ion exchange and adsorption appear as valuable applications, since the uptake of ions or molecules by such materials may produce measurable differences on its photoluminescent spectra and thus making them promising chemical sensors. Nonetheless, it is important to know in advance the number of RE/Ln sites optically available in each material (see Table 1). Sorption processes may be even more relevant when the solid has a layered structure, since the space between adjacent layers can host different ions or molecules that may act as Ln-antennae or efficient energy bridges across them [20]. This was clearly observed in the photoluminescence studies accomplished

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