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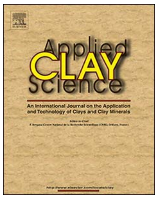

Research paper

New phosphors synthesised by ion exchange of a metakaolin-based geopolymer

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ABSTRACT

A geopolymer prepared from dehydroxylated kaolinite-type clay was used as a host for trivalent rare earth ions to produce new photoluminescent materials. Sm^{3+} and Eu^{3+} ions were individually incorporated into the geopolymer host by ion exchange, partially replacing the charge-balancing K^+ ions. The resulting materials were characterised by XRD, SEM/EDS, ^{27}Al and ^{29}Si MAS NMR and PIXE, and their luminescence behaviour was determined by photoluminescence spectroscopy. In addition to the characteristic photoluminescence of the Sm^{3+} and Eu^{3+} ions, the geopolymer host exhibited broad-band photoluminescence peaking at 440 nm under 372 nm excitation. The use of the clay-based geopolymer host permitted a higher concentration of rare earth ions to be incorporated compared with a previously reported chemosynthetic aluminosilicate inorganic polymer host, resulting in rare earth photoluminescence of increased intensity. A further advantage of the clay-based geopolymer phosphor is its ease of synthesis and cost-effectiveness compared with the chemosynthetic aluminosilicate inorganic polymer host.

1. Introduction

Since the end of the 19th century, the applications for luminescent materials have grown with the advance of lighting and visualisation technology, making these materials increasingly important in modern devices (Feldmann et al., 2003; Filho et al., 2015). Inorganic luminescent materials, or phosphors, normally consist of a host material containing luminescent activators such as rare earth ions. The host must allow the activators to be effectively incorporated and dispersed, and the chemical and thermal stability of the host is an important factor for real-world applications, as well as considerations such as the cost of production and environmental factors. The performance of the phosphor depends on the host environment, including any lattice defects and impurities, and the coordination sites provided by the host affect the energy and probability of particular luminescent transitions of the activator (Ropp, 2004; Werts, 2005). New host materials, including single crystals, powders, thin films, nanostructured materials, glasses, and glass ceramics are continually being developed to improve on those used in current devices and to meet the requirements of new applications, but many of these require specialised synthesis methods and reagents. Aluminosilicate geopolymers, which can readily be synthesised cost-effectively from dehydroxylated clay, have been extensively studied (Kuenzel et al., 2013; Tchakoute et al., 2015; Douiri et al., 2017). The many applications of clay-based geopolymers (MacKenzie, 2017) include the remediation of hazardous metal ions (El-Eswed et al., 2017) and as materials for stabilising and preserving items of cultural heritage (Clausi et al., 2016), but very few studies have been reported on the use of geopolymers as hosts for luminescent phosphors. Geopolymers have been suggested to be structurally similar to zeolites (Provis et al., 2005), and since these have successfully been used as hosts for luminescent materials (Kynast and Weiler, 1994; Jüstel et al., 2001; Yang et al., 2011; Serykh and Rozhdestvenskaya, 2015), it is likely that geopolymers may be similarly active as luminescence hosts, but with the advantage of being simpler and more cost-effective to synthesise than zeolites. Clay-based geopolymers have been successfully demonstrated as supports for a commercial phosphor ($Sr_2MgSi_2O_7$:$Eu^{2+}Dy^{3+}$) (Gasca-Tirado et al., 2011), and the ion-exchange properties of a chemosynthetic aluminosilicate inorganic polymer have successfully been exploited to insert photoluminescent rare earth ion activators into the structure (Rogers et al., 2017a). In this paper we report the use of a similar ion-exchange technique to synthesise Eu^{3+} and Sm^{3+} phosphors from inexpensive and readily-produced clay-based geopolymers and an investigation of their structure and photoluminescence behaviour.

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2. Experimental

2.1. Synthesis

The potassium geopolymer host was prepared from a kaolinite-type New Zealand halloysite clay (Imerys NZ Premium Grade) which was dehydroxylated at 600 °C overnight. This was reacted with a solution of potassium silicate (Ineos Silicas, grade K66) in KOH, to give a molar composition of $SiO_2/Al_2O_3 = 3.16$, $K_2O/SiO_2 = 0.34$, $H_2O/K_2O = 16.2$. After stirring for 10 min. The mixture was transferred to a mould and cured at 60 °C for 48 h. The hardened geopolymer was finely ground, after which the rare earth activator ions were introduced by exploiting the ion exchange properties of the geopolymer as follows.

The ground geopolymer was washed by stirring in distilled water (100 mL per gram of geopolymer) for 24 h. to remove excess KOH, recovered by vacuum filtration and dried overnight at 120 °C. 1.0 g of the washed and dried potassium aluminosilicate geopolymer was added to 10 mL of a 0.05 mol dm^{-3} solution prepared by dissolving $SmCl_3{\cdot}6H_2O$ (Santa Cruz Biotechnology, > 97%) or $EuCl_3{\cdot}6H_2O$ (Sigma Aldrich, 99.99%) in distilled water. After stirring for 24 h. the ion-exchanged geopolymers were filtered off and dried at 120 °C. This ion exchange process exploits the presence of cations within the geopolymer structure which balance the negative charge in the vicinity of each aluminium atom in the structure, resulting from its conversion to a tetra-coordinated aluminate unit (MacKenzie, 2017). These charge-balancing cations, which are K^+ in the present initially-formed geopolymer, are exchangeable with other cations (O'Connor et al., 2010), and being strongly held electrostatically within the geopolymer structure of which they are a part, are stable to leaching.

2.2. Sample characterisation

The Al, Si, K and rare earth contents of the samples were determined by Particle Induced X-ray Emission (PIXE). Pressed pellets of the samples were exposed to a 2.5 MeV beam of protons generated in a Van de Graaff accelerator and the characteristic emitted K or L X-rays were detected using a Si(Li) detector, amplified and recorded in a pulse height analyser. The overlapping peaks of the resulting PIXE spectra were deconvoluted with high accuracy using quantitative X-ray analysis software. PIXE was the analytical method of choice since the use of a proton beam makes it more sensitive than EDS by at least two orders of magnitude.

The powdered samples were analysed by X-ray powder diffraction (XRD) (PANalytical X'Pert PRO MPD diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and 0.04 rad incident and diffracted beam Soller slits, operated at 45 kV, 40 mA with 0.013°2Θ step size and 0.020°2Θ/s scan speed) and ^{27}Al and ^{29}Si solid state magic angle spinning nuclear magnetic spectroscopy (MAS NMR) using a Bruker Avance 500 spectrometer at a magnetic field of 11.7 T. The ^{27}Al MAS NMR measurements were made at a frequency of 130.224 MHz with a 1 μs pulse and 1 s delay while spinning the sample at 10–12 kHz in a 4 mm Doty Scientific MAS rotor. A 1 mol dm^{-3} aluminium nitrate solution was used as the reference. The ^{29}Si MAS NMR spectra were acquired at a frequency of 99.926 MHz with a 6 μs pulse and a 30 s delay in a 5 mm Doty Scientific MAS rotor spun at 6 kHz. The spectra were referenced against tetramethylsilane (TMS).

The powdered samples were mounted on aluminium stubs with adhesive carbon tape and coated with 20 nm platinum for investigation by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a JEOL JSM 6610 LV scanning electron microscope equipped with an energy dispersive X-ray spectrometer. The microscope was operated in high vacuum mode at an accelerating voltage of 15 kV, a working distance of 10 mm and a spot size of 60 nm.

Table 1
Atomic compositions of the geopolymer host and the Sm^{3+}- and Eu^{3+}- exchanged samples, determined by PIXE (RE = rare earth).

Sample	K/Al	RE/Al	K/Si	RE/Si	Si/Al	RE (wt%)
Geopolymer before washing	0.89	0	0.63	0	1.41	0
Geopolymer host, washed	0.69	0	0.50	0	1.38	0
Sm^{3+}-exchanged geopolymer	0.48	0.18	0.33	0.123	1.45	7.99
Eu^{3+}-exchanged geopolymer	0.49	0.18	0.33	0.124	1.47	8.00

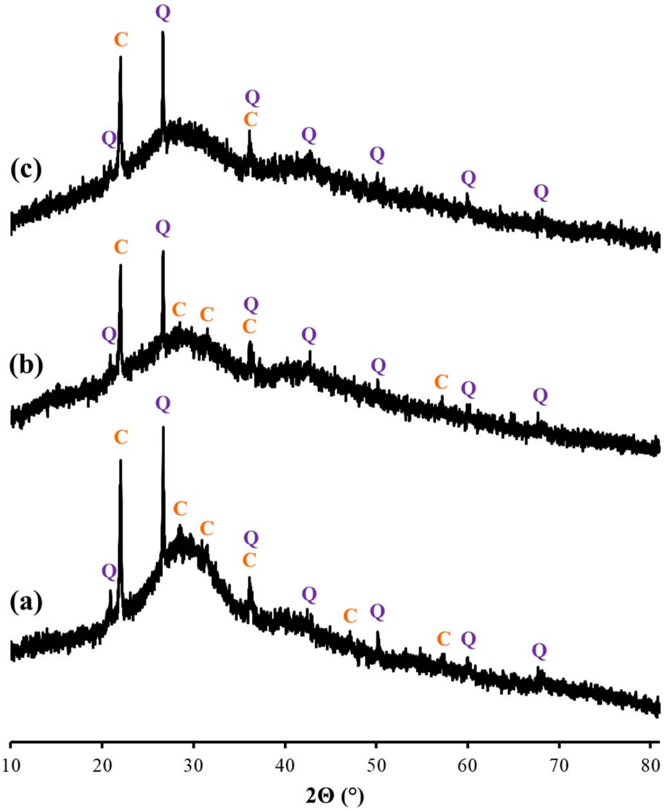

Fig. 1. XRD traces of (a) unexchanged geopolymer host, (b) Sm^{3+}-exchanged geopolymer, (c) Eu^{3+}-exchanged geopolymer. Q = quartz (PDF 01-070-7344), C = cristobalite (PDF 00-039-1425).

2.3. Photoluminescence measurements

The photoluminescence measurements were made on 12 mm dia. pellets pressed from 0.30 g of powder at 6 t pressure. The excitation and emission spectra of these samples were measured at room temperature using a Horiba Jobin Yvon Flurolog 3 spectrofluorometer with a 450 W xenon arc lamp and were corrected for variations in the lamp intensity.

3. Results and discussion

3.1. Sample characterisation

Table 1 shows the atomic ratios of the as-synthesised geopolymer both before washing (as-synthesised) and after washing, determined by PIXE analysis. The change in the K/Al ratio indicates that approximately 45% of the K^+ in the original geopolymer was either washed from the sample during synthesis, or exchanged by rare earth (RE) ions or H_3O^+. Based on the RE/Al ratio, 20% of the original K^+ was replaced by Sm^{3+} or Eu^{3+}. This is higher than the theoretical 15% expected if trivalent rare earth ions replace K^+ in a 1:3 ratio with 55% of the K^+ remaining, but the total charge provided by the K^+ and RE^{3+} ions is close to the total required to balance the charge associated with