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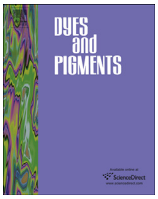

Synthesis and characterization of environmentally benign inorganic pigments with high NIR reflectance: Lanthanum-doped $BiFeO_3$

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ABSTRACT

A new environmentally benign near-infrared reflectance pigment based on $BiFeO_3$ doped with La^{3+} was described. The pigments of the formula $Bi_{1-x}La_xFeO_3$ (x = 0, 0.1, 0.2, 0.3, 0.4) were characterized by XRD, FE-SEM, TG-DTA, UV-vis-NIR spectrophotometer and CIE $L^*a^*b^*$ color scales. The results reveal that the pigments crystallized at 600 °C with particle size less than 70 nm. The substitution of La^{3+} for Bi^{3+} in $BiFeO_3$ shift the color from dark brown to reddish brown and the band gap decrease from 2.24 to 2.03 eV due to O_{2p}-Fe_{3d} charge transfer transitions. The near-infrared solar reflectance of the powdered pigments increased with the increase of progressive doping of La^{3+} for Bi^{3+}. The pigment coated on concrete cement substrate exhibit higher near-infrared solar reflectance ($R^* \geq 44.1\%$) than conventional coating of similar color. Moreover, the thermal and chemical stability of the pigments were also evaluated. In conclusion, the pigments have the potential to be applied as "cool pigments".

1. Introduction

Inorganic colored pigments with high near-infrared (NIR) reflectance are widely used in various fields for decorative and protective coatings (e.g. rooftop coverings, vehicle coatings, or ceramics, glasses coloring) due to their high chemical and thermal stability, more importantly, protective capability against solar heat radiation of this NIR reflective materials [1]. Approximately 5% of solar energy reaches the earth in the form of ultraviolet radiation (UV: 200–400 nm), 43% is constituted by visible radiation (VIS: 400–700 nm), and 52% is occupied by near-infrared radiation (NIR: 700–2500 nm) [2], where the heat producing area is in the NIR region. Thus, inorganic pigments with high NIR reflectance can be employed as cool pigments and applied to roof coatings, improving internal thermal comfort levels to save the cooling energy in hot seasons [3,4]. Ultimately, increasing the reflection of infrared energy reduces the heat accumulation [5] resulting in a reduction on the load of the cooling system, and is an environmentally benign way [6].

Pigment color is closely relevant to the effect of heat reflection. White materials have the best performance in heat reflection [7]. For instance, TiO_2, with high solar reflectance of ~87%, is often used as cool colored materials [8]. Nevertheless, white pigment has the disadvantages of light pollution, poor stain resistance, monochrome, etc, and thus the demand for function and aesthetic is unsatisfactory for people. Accordingly, many colored pigments with high NIR reflectance have been developed, but many of these pigments encompass toxic heavy metal elements such as Co, Pb, Cd, and Cr [9–11]. Their use is restricted by the current environmental regulations. Thus there is a strong incentive to develop new NIR reflective pigments which are less hazardous, durable, and could serve as excellent alternatives for replacing traditional toxic and heavy metal based pigments that threat health and the environment.

$BiFeO_3$ is a very good material for both physical and chemical properties. The crystal structure of $BiFeO_3$ is rhombohedral distorted perovskite structure with space group *R*3*c* [12,13]. $BiFeO_3$ has been intensively investigated due to it has high ferroelectric Curie temperature (T_C = 830 °C) and G-type antiferromagnetic Neel temperature (T_N = 370 °C) [14,15]. In addition to the multiferroic nature, $BiFeO_3$ possesses interesting optical properties [16] and therefore also used as UV and visible light photocatalyst for water splitting and degradation of organic pollutants due to the narrower band gap (2.0–2.8 eV) than most classical perovskite materials. Substitution with rare-earth elements at Bi-site of $BiFeO_3$ is an alternative efficient way to induce the lattice distortion to enhance the dielectric and magnetic properties [17–19]. Furthermore, dopants based on rare earth elements in mixed oxide offer an

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opportunity to tune the color response through manipulation of energy gaps and delocalization phenomenon in conduction and valence bands [20], which can alter the optical properties of the material. The multiferroic of lanthanides doped $BiFeO_3$ have been extensively studied [21–24], However, few researches have investigated their chromatic and NIR reflection properties as a pigment. Owing to do not contain toxic heavy metal elements and unique optical properties [25], they have a wide range of prospects in industrial applications, including inorganic pigments for ceramic glazes and architectural coatings [26].

In this paper, we synthesized La^{3+} doped $BiFeO_3$ nanoparticles by sol-gel method and investigated their properties as inorganic pigment for the first time. The new pigments of the formula $Bi_{1-x}La_xFeO_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) were characterized with respect to structure, morphology, chromaticity, and NIR reflective properties. In particular, these new pigments were also been coated on concrete cement and compared the NIR reflectance with the conventional pigment coating. Moreover, the thermal and chemical stability of the pigments were evaluated.

2. Experimental

2.1. Materials and methods

Samples based on $Bi_{1-x}La_xFeO_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) were prepared by sol-gel procedure, using Bi $(NO_3)_3 \cdot 5H_2O$, Fe $(NO_3)_3 \cdot 9H_2O$, La $((NO_3)_3 \cdot 6H_2O$, citric acid (CA), acrylamide (AM) and glucose as precursors). All reagents were of analytical grade and without further purification. A scheme of the general preparation of the samples is shown in Fig. 1. Stoichiometric amounts of Bi $(NO_3)_3 \cdot 5H_2O$, Fe $(NO_3)_3 \cdot 9H_2O$ and La $(NO_3)_3 \cdot 6H_2O$ were dissolved in dilute HNO_3 solution. After the solution became clear, a stoichiometric amount of CA, which was used as a chelating agent to complex the cations, was added to the solution in the mole ratio 3:1 with respect to the cations (Bi^{3+}, Fe^{3+} and La^{3+}). Subsequently, AM was added to the solution in the mole ratio 4:1 with respect to the cations (Bi^{3+}, Fe^{3+} and La^{3+}) for control the particle size of the powders. Finally, a small amount of glucose was dissolved. The resultant solution was heated at 80 °C in water and stirred continuously until a homogeneous gel was obtained. The gel was dried at 100 °C to obtained xerogel. Finally, the xerogel was grinded into powder and succeeding calcined at 600 °C for 4 h to produce powdered samples.

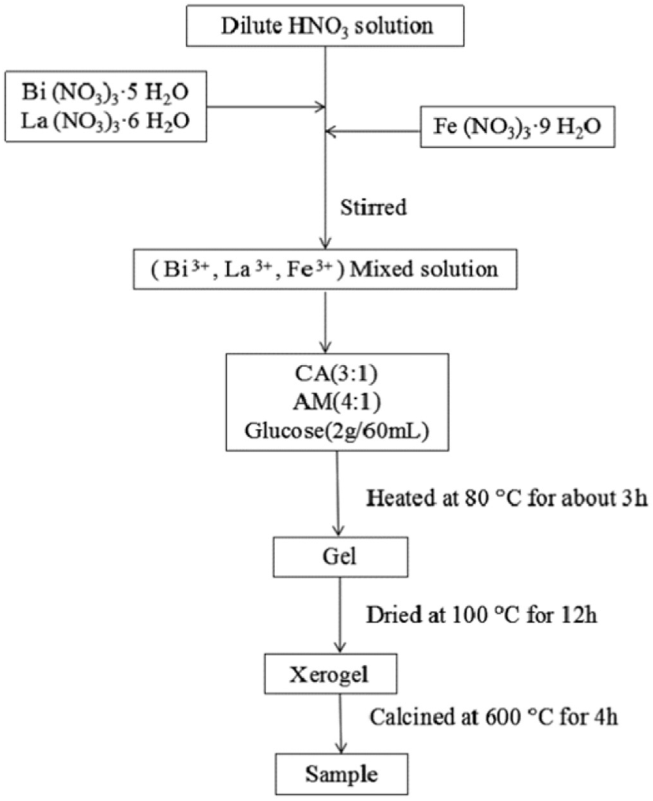

Fig. 1. Scheme for the synthesis procedure.

2.2. Characterization techniques

Phase analysis of the samples was characterized by powder X-ray diffraction ($\lambda = 0.154060$ nm) in an Advanced Diffract meter (Bruker, D8) with Ni-filtered Cu Kα radiation. Data were collected by step-scanning from $2\theta = 10–70°$ with a step size of 0.05° and 5 s of counting time at each step. Particle morphological analysis of the samples was performed by a field emission scanning electron microscopy (FE-SEM) (HITACHI, S-4800Π FE-SEM), with an acceleration voltage of 15.0 kV. The composition and the quantitative analysis of the samples was tested using inductively coupled plasma emission spectrometer (ICP) (PerkinElmer, Optima 7300 DV). The operation parameters was summarized in Table 1.

Table 1
ICP operating parameters.

Parameters	
Plasma gas flow rate (L min−1)	15
Auxiliary gas flow rate (L min−1)	0.2
Nebulizer gas flow rate (L min−1)	0.8
RF power (W)	1300
Pump flow rate (mL min−1)	1.5
Wavelength (nm)	Bi 223.061 La 408.672 Fe 238.204

The diffuse reflectance of the samples was measured with an UV-vis-NIR spectrophotometer (Shimadzu, UV-3600 with an integrating sphere attachment) in the visible region (300–700 nm) and NIR region (700–2500 nm). $BaSO_4$ was used as a reference. From the diffuse reflectance (R) spectra obtained with the spectrophotometer, the samples absorption edge and the corresponding band gap energy can be calculated by the Kubelka-Munk reemission function:

$$F(R) = \frac{(1 - R)^2}{2R} \tag{1}$$

where R represents the diffuse reflectance of the sample at infinite thickness.

The color parameters of the samples were obtained from Konica Minolta (CM-2500d) with an integrating sphere attachment. The CIE L^* a^* b^* color space [27] was used to describe the composites color properties. Each color in this system has a unique position defined by Cartesian coordinates with respect to the axes L^*, a^*, and b^*. Two of the mutually orthogonal axes, a^* and b^*, represent the hue or color dimensions. The third axis, L^* is perpendicular to $a^*$and b^* plane and the value represents the lightness or darkness of the color ($L^* = 0$ for black and $L^* = 100$ for white). Positive a^* value related to red color; negative value, to green. Positive b^* value related to yellow color; negative value, to blue [28]. The parameter C^* (Chroma) expresses saturation of the color and is defined as the formula: