Optical Materials 47 (2015) 143–148

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

The photoluminescence properties of tri-colour silicoaluminate phosphors prepared from oil shale ash

Hui Zhang [a], Yanhua Song [a], Ye Sheng [a], Keyan Zheng [a], Shizhou Ding [b], Bo Yuan [a], Xuechun Xu [c], Haifeng Zou [a,*]

[a] College of Chemistry, Jilin University, Changchun 130012, PR China
[b] Shandong Megavision Membrane Technology & Engineering Co., Ltd., Beijing 100084, PR China
[c] College of Earth Sciences, Jilin University, Changchun 130026, PR China

ARTICLE INFO

Article history:
Received 3 June 2015
Received in revised form 28 June 2015
Accepted 7 July 2015
Available online 13 July 2015

Keywords:
Oil shale ash
Silicoaluminate
Tri-colour phosphors
Luminescence
Comprehensive utilization

ABSTRACT

In this paper, high value-added tri-colour phosphors $Ba_{0.96}Mg_{1.88}Si_2O_7$:0.02$Eu^{2+}$, 0.02$Dy^{3+}$, 0.12$Mn^{2+}$; $CaSr_{0.995}SiO_4$:0.005Eu^{2+} and $Ba_{0.91}MgAl_{10}O_{17}$:0.09Eu^{2+} were prepared using the white carbon black (hereinafter referred to as WCB) and alumina extracted from oil shale ash as raw materials. The structure and luminescence properties of the samples were characterized by X-ray diffraction (XRD) and photoluminescent spectra. The results show that the red and green phosphors synthesized by WCB exhibited much weaker emission than the phosphors synthesized by pure chemical reagent silica, which is mainly due to the high content of iron in the WCB. After purifying the WCB under laboratory conditions, the luminescence properties were improved and close to that of pure chemical reagent. By comparing with the emission of the samples synthesized with chemical reagents, the results show that the products extracted from oil shale ash can be applied to synthesize luminescent materials which have potential applications in white-light ultraviolet (UV)-LED field.

1. Introduction

Oil shale is a type of alternative energy and possesses expanded potential under energy crisis. Therefore, more and more oil shale has been mined and applied for several decades [1,2]. The exploration indicates that China is rich of shale oil resources. It was reported that there are 2432 million tons of the mined reserves, and 120 million tons of refined oil shale in China [3]. After oil shale being refined, a large amount of oil shale ash is abandoned, resulting in serious environment pollution and resources waste [4,5]. Generally, oil shale ash mainly consists of aluminum, iron and silicon compounds and less calcium, magnesium, sodium, potassium and titanium compounds [6,7]. Several methods have been reported to make full use of these resources, such as producing nanoscale silica powders [8], silica aerogel [9], zeolite [10], filter media [11], building material [12]. However, higher valued products are desirable.

At present, attention on energy saving and green issues gives a boost to the research of white light-emitting diodes (w-LEDs) for lighting, due to their advantages of high efficiency, long lifetime, low power consumption and environment friendly characters [13,14]. Usually, the widely used means to generate white light in white LEDs is combining UV or blue LED chip with rare earth ion doped phosphors, which are usually defined as phosphor converted WLEDs (pc-WLEDs) [15]. The emission colour of pc-WLEDs depends only on the phosphors [16], and thus the design and development of tri-colour phosphors which can be excited by UV or blue LEDs has been in numerous studies.

As mentioned above, oil shale ash is rich of alumina and silica. Both of alumina and silica are the appropriate raw materials for producing phosphors [17–20]. It makes it possible to utilize oil shale ash for producing luminescent materials. However, very few studies on this issue have been done until now. In this paper, we prepared phosphors with oil shale ash, studied their luminescence and compared with the products prepared by chemical reagents.

2. Experimental

2.1. Materials and preparation

The raw reactants were analytical reagent grade (99.90%) $CaCO_3$, $SrCO_3$, Al_2O_3, SiO_2, $BaCO_3$, MgO, $MnCO_3$ and spectrographically pure (99.99%) Eu_2O_3, Dy_2O_3. The oil shale ash was obtained

* Corresponding author.
E-mail address: haifengzou0431@gmail.com (H. Zou).

http://dx.doi.org/10.1016/j.optmat.2015.07.015
0925-3467/

Table 1
The sintering conditions of all samples.

Phosphors	Sintering temperature (°C)	Sintering time (h)	Reducing atmosphere
$CaSr_{0.995}SiO_4$:0.005Eu^{2+}	1350	3	H_2/N_2
$Ba_{0.96}Mg_{1.88}Si_2O_7$:0.02$Eu^{2+}$, 0.02$Dy^{3+}$, 0.12$Mn^{2+}$	1200	5	H_2/N_2
$Ba_{0.91}MgAl_{10}O_{17}$:0.09Eu^{2+}	1400	2	H_2/N_2

from Daqing Mining Group Co., Ltd. (China), and the raw material WCB (SiO_2) and Al_2O_3 were extracted from the oil shale ash.

The stoichiometric amount (which has been corrected by the purity in the Table 3) reactants were mixed and ground in an agate mortar, then transferred into a corundum crucible, and sintered in a tubular furnace under a reducing atmosphere under different conditions. The sintering details are listed in Table 1.

In order to obtain better luminescent materials, the WCB extracted from oil shale ash should be purified. The purification process of the WCB is as followed:

Firstly, the WCB was dissolved in 30% sodium hydroxide aqueous solution. Then it was refluxed in a 100 °C oil bath for 3 h, thus all silica was converted to sodium silicate. Secondly, hydrochloric acid was added to the sodium silicate solution until the pH value of the solution is 1–2, which results in sodium silicate converted to insoluble silica. Finally, the insoluble silica was filtrated, dried and calcined to get purified silica.

2.2. Characterization

The synthesized samples were analyzed by X-ray power diffractometer (Rigaku D/Max-B II), with Cu Kα radiation (λ = 0.15405 nm). The excitation and emission spectra were measured by a Jobin Yvon FluoroMax-4 equipped with a 150 W xenon lamp as the excitation source. The luminescence decay curves of the phosphors were measured by FLS920 and the excitation source was 350 W xenon lamp. All the above experiments were recorded at room temperature. The component analysis of WCB and reagent silica were measured by an energy dispersive micro XRF spectrometer (μEDX-1200, Shimadzu Co.) equipped with Rhodium (Rh) X-ray tube with a Ni filter as the primary X-ray filter. And the component analysis of Al_2O_3 was checked by the Atomscan Advantage inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

3. Results and discussion

3.1. The basic properties of WCB and alumina extracted from oil shale ash

The oil shale ash is rich of silica, alumina, iron oxide and so on. Table 2 is the components of Daqing Oil Shale Ash (wt.%). And our starting materials silica and alumina are extracted from this oil shale ash.

Fig. 1.1 is the photos of the WCB and alumina extracted from oil shale ash. Both of them are white powder. And in Fig. 1.2, it is the SEM images of original, annealed, purified WCB particles, reagent silica, alumina extracted from OSA and reagent alumina. The length of the annealed WCB particles (about 200 nm) is longer than the original WCB particles (about 130 nm). But after purification, it decreases to around 180 nm. However, alumina from oil shale ash is floccule, which is much different from reagent alumina. It maybe affects the luminescence properties of the optical materials made by OSA alumina.

Table 2
The mainly components in OSA (wt.%).

Site	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI
Daqing	63.58	16.69	5.47	5.12	2.51	1.68	1.02	2.24

Table 3
The element compositions of chemical reagent silica and WCB extracted from oil shale ash (%).

Sample	SiO_2	Fe_2O_3	LOI
Reagent silica	99.52	0.06	0.05
Original WCB	94.59	0.27	2.91
Annealed WCB	95.36	0.28	2.08
Purified WCB	93.57	0.12	4.80
Purified WCB twice	95.99	0.07	3.15

3.2. $CaSr_{0.995}SiO_4$:0.005Eu^{2+} green phosphor for LED

Fig. 2.1 shows the XRD patterns of $CaSr_{0.995}SiO_4$:0.005Eu^{2+} samples prepared by WCB extracted from oil shale ash and by reagent silica. It is clearly observed that all of the diffraction peaks are well coincident with JCPDS standard card 77-1619, which indicates that these samples are single phases and it is feasible to use WCB extracted from oil shale to prepare the $CaSrSiO_4$ crystal.

The photoluminescence spectra of $CaSr_{0.995}SiO_4$:0.005Eu^{2+} synthesized with WCB and reagent silica are shown in Fig. 2.2. Under the excitation of 365 nm, the two phosphors show green emission peaking at 502 nm from 450 nm to 650 nm. But the emission intensity of $CaSr_{0.995}SiO_4$:0.005Eu^{2+} synthesized with chemical reagent is stronger far away than that synthesized by the WCB. It is inferred that the purity of WCB is low and the impurity has the quenching effect. So the element compositions were analyzed by XRF in detail as shown in Table 3 (the experimental data are shown in Figs. S1–S3 and Tables S1–S3). The content of iron oxide in reagent silica is only 0.06%, but in WCB, it is 0.27%. And LOI, short for loss on ignition, is also too high in WCB. Because iron quenches the luminescence properties [21,22], it is believed that the high contents of iron has an effect on the luminescent properties. Another noteworthy point is the large changes in LOI between the original WCB (2.91) and purified WCB (4.80). TGA analysis (Fig. 2.3) was assisted to explain this phenomenon. There are two obvious weight loss in the purified WCB compared with the reagent silica. The first one (from 50 °C to 150 °C) is due to the decomposition of H_2SiO_3. The second one between 150 °C and 850 °C is attributed to the evaporation of Si–OH. Both of the H_2SiO_3 and the Si–OH were produced by the transition from Na_2SiO_3 to WCB in the purification process. Because of the superfluous HCl in the purification process, some H_2SiO_3 and Si–OH were preserved. That is why the weight loss is obvious in the purified WCB but unconspicuous in the annealed WCB and reagent silica. According to the above results, our experiment conditions were improved.

After calcining and purifying the WCB, the new spectra were acquired in Fig. 2.4. The luminescent intensity of the phosphor made by annealed WCB has a little raise but it still has a large gap with standard. Then XRD patterns of all the samples made by WCB were used to confirm that why the Eu^{2+} emission intensity is higher in the annealed WCB as compared to original WCB. The results are shown in Fig. 2.5. The crystallinity of the $CaSr_{0.995}SiO_4$:0.005Eu^{2+} phosphor made by annealed WCB is stronger than that made by original WCB. It may due to the more regular morphology of annealed WCB compared with original WCB. Moreover, the luminescent intensity of the phosphor made by purified WCB is very close to that made by reagent silica. It is inferred that it is feasible to use the WCB extracted from oil shale