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# Spontaneous $Sm^{3+} \rightarrow Sm^{2+}$ reduction ability of $MAl_2Si_2O_8$ (M = Sr, Ba): Sm

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## ABSTRACT

In air atmosphere, the spontaneous reduction abilities of $Sm^{3+} \rightarrow Sm^{2+}$ in Sm ions doped monoclinic $SrAl_2Si_2O_8$ (SASO) and $BaAl_2Si_2O_8$ (M-BASO) as well as hexagonal $BaAl_2Si_2O_8$ (H-BASO) are investigated. Sm ions doped $MAl_2Si_2O_8$ (M = Sr, Ba) samples were synthesized using Pechini-type sol-gel technology and sintered in air atmosphere and reducing condition, respectively. By comparing the photoluminescence properties of Sm doped $MAl_2Si_2O_8$ (M = Sr, Ba) calcined in air with that in reducing condition, the spontaneous reduction of $Sm^{3+} \rightarrow Sm^{2+}$ can be detected only in the host lattice H-BASO. The essential that makes the reduction of $Sm^{3+}$ to $Sm^{2+}$ was investigated by calculating their chemical bonds parameter quantitatively. The important key environmental factor of $Ba^{2+}$ in H-BASO is the largest among the three samples $MAl_2Si_2O_8$. It indicates that the hexagonal H-BASO sample is the easiest one to realize the spontaneous reduction of $Sm^{3+} \rightarrow Sm^{2+}$ among Sm doped $MAl_2Si_2O_8$ (M = Sr, Ba) samples. The needed energy transferring one electron of the ligand to the central ions $Sm^{3+}$ in H-BASO:Sm is the lowest. The theoretical analysis agrees well with the experimental result. Our work provides with the theoretical and experimental foundation for the spontaneous reduction of trivalent samarium in the crystals.

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## 1. Introduction

Divalent rare earth ions ($Eu^{2+}$, $Sm^{2+}$) have been widely used as activators in phosphors [1–10]. To obtain the materials activated by divalent rare earth ions, usually, the reduction of trivalent to divalent rare earth ion must be realized since the raw material of the rare-earth source is usually trivalent ($Eu_2O_3$, $Eu(NO_3)_3$, $Sm_2O_3$, $Eu(NO_3)_3$). From the chemical point of view, the reduction of an element needs a reducing environment. However, some trivalent rare earth ion doped in some matrices could be reduced into divalent rare earth ion when these samples are prepared in air, not in a reducing atmosphere ($H_2$-$N_2$ or CO) [6,11–18]. It is abnormal and interesting. Up to now, this “spontaneous reduction” has been found in aluminates ($Sr_4Al_{14}O_{25}$:Eu [12], $BaAl_2O_4$:Eu [19]), borates ($SrB_4O_7$:Eu or Sm or Yb [7,20,21], $SrB_6O_{10}$:Eu [21], $BaB_8O_{13}$:Eu [20], $CaB_2O_4$:Eu [13]), haloborate ($Sr_2B_5O_9Cl$:Eu [22,23]), boraphosphates ($MBPO_5$, M = Ca, Sr or Ba [21]), germinate ($Zn_2GeO_4$:Eu [24]), phosphates ($Ba_3(PO_4)_2$ [25], $NaCaPO_4$ [17]), silicates ($BaMgSiO_4$ [11]), aluminosilicate ($CsAlSi_2O_6$:Eu [18]), sulfate ($BaSO_4$ [26]). Except for the “self-reduction” of the rare earth ions (RE), some non-RE ions also show this property, such as $Ca_2P_2O_7$:Bi and $Sr_2P_2O_7$:Bi [27,28], Bi ion-doped strontium borates [29–31].

The alkaline-earth feldspars $MAl_2Si_2O_8$ (M = Ca, Sr, Ba) were reported to be very suitable hosts for $Eu^{2+}$ ions [32–35]. The spontaneous reduction of $Eu^{3+} \rightarrow Eu^{2+}$ in $CaAl_2Si_2O_8$, $SrAl_2Si_2O_8$ and hexagonal $BaAl_2Si_2O_8$ has been found when heated in air at high temperature [15,36–38]. It has been reported that fours conditions are necessary to realize the spontaneous reduction [19–21]. (1) there is not oxidizing ions in the crystal; (2) trivalent rare earth ions substitutes a divalent cation site; (3) the substituted cation and this trivalent rare earth ion have similar radii; and (4) the host has a rigid structure, that is, having tetrahedral anion groups, such as $SiO_4$, $AlO_4$, $BO_4$ and $SO_4$. The $MAl_2Si_2O_8$ (M = Ca, Sr, Ba) crystals meet these conditions. Also, the spontaneous reduction of both $Eu^{3+} \rightarrow Eu^{2+}$ and $Sm^{3+} \rightarrow Sm^{2+}$ has been realized in the crystal $SrB_4O_7$ simultaneously [20]. These statements prompt us to investigate samarium-doped $MAl_2Si_2O_8$ (M = Sr, Ba) crystals and it may also be expected that $Sm^{3+}$ can be reduced to $Sm^{2+}$ prepared

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in air. In our experiment, we choose the monoclinic $SrAl_2Si_2O_8$ and $BaAl_2Si_2O_8$ as well as hexagonal $BaAl_2Si_2O_8$ as the hosts because there is only one kind of $M^{2+}$ site in these $MAl_2Si_2O_8$ crystal structure [39]. In a reducing atmosphere ($H_2$-$N_2$ or CO), $Sm^{3+}$ or $Sm^{2+}$ doped $MAl_2Si_2O_8$ (M = Sr, Ba) crystals can efficiently emit light and their photoluminescence (PL) properties can provide the sufficient evidence for the existence of $Sm^{3+}$or $Sm^{2+}$ at room temperature [39,40]. According to the above achievements, we expect to investigate the spontaneous reduction ability of $Sm^{3+}\rightarrow Sm^{2+}$ in Sm ions doped $MAl_2Si_2O_8$ (M = Sr, Ba) through measuring their PL properties.

In this paper, the spontaneous reduction ability for samarium from trivalent to divalent in Sm-doped $MAl_2Si_2O_8$ (M = Sr, Ba) crystals is reported systematically. The PL properties of Sm ions are studied. Different spontaneous reduction ability is investigated. The essential factor influencing the reduction ability of $Sm^{3+}$ was discussed quantitatively. Our work provides with the theoretical and experimental foundation for the spontaneous reduction of trivalent samarium in the crystals.

## 2. Experimental section

### 2.1. Sample preparation

The $MAl_2Si_2O_8$ (M = Sr, Ba) powder samples were prepared by a pechini-type sol-gel process, which can give the highest possible homogeneity for the material [41]. The doping level of $Sm^{3+}$ was kept to be 5.0mol % in $MAl_2Si_2O_8$:Sm. The mixtures were heated in a hydrogen-nitrogen (5%$H_2$+95% $N_2$) atmosphere and in air, respectively.

The raw materials were $Sm_2O_3$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Al(NO_3)_3\cdot 9H_2O$, tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS) and citric acid as the chelating agent. The preparation of solid gels can refer to the experimental part of references [39,40]. The solid gels were prefried at 1200 °C for 4 h. After being fully ground, MASO (M = Sr, Ba): Sm samples were pressed into pellets, which were annealed at 1400–1600 °C for 3 h in the reducing atmosphere and in air for 3 h, respectively.

### 2.2. Characterizations

The phase purity of the as prepared phosphor was checked by powder x-ray diffraction (XRD) analysis by using a D/MAX 2500 instrument (Rigaku) with a Rint 2000 wide angle goniometer and Cu K$\alpha$1 radiation ($\lambda$ = 1.54056 A) at 40 kV and 100 mA. The measurements of PL and photoluminescence excitation (PLE) spectra were performed by using a fluorescence spectrophotometer (Photon Technology International) equipped with a 60 W Xe-arc lamp as the excitation light source. All the measurements were taken at room temperature.

## 3. Theoretical method

The dielectric theory of complex crystals was used to calculate the chemical bond parameters of inorganic compounds quantitatively [42,43]. This theory was developed based on the theory developed by Phillips and Van Vechten [44] (PV). The crystal structure and the detail calculation method of $MAl_2Si_2O_8$ (M = Sr, Ba) can be referred to reference [40].

## 4. Results and discussion

### 4.1. Crystal phase formation

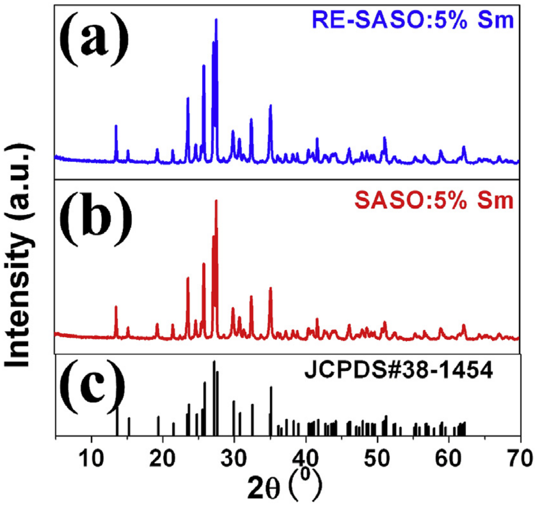

**Fig. 1.** XRD patterns of Sm-doped $SrAl_2Si_2O_8$ samples prepared in reducing atmosphere (a) and in air condition (b) as well as the standard card of $SrAl_2Si_2O_8$ (c).

Fig. 1(a) and (b) show X-ray diffraction (XRD) patterns of $SrAl_2Si_2O_8$:Sm in the thermal reducing atmosphere (5% $H_2$+95% $N_2$) (Re-SASO:Sm) and $SrAl_2Si_2O_8$:Sm samples calcined in air (SASO:Sm), respectively. Unless otherwise stated, “Re-” means that the sample was calcined in reducing atmosphere. Their patterns can be well indexed according to the Joint Committee on Powder Diffraction Standard (JCPDS) No. 38-1454 ($SrAl_2Si_2O_8$) selected in the International Centre for Diffraction Data (ICDD) database.

The pure hexagonal and monoclinic phases of $BaAl_2Si_2O_8$:Sm, which can be named as H-BASO and M-BASO, calcined in air and under reducing atmosphere, were synthesized successfully, respectively. As can be shown in Fig. 2, the XRD patterns of M-BASO (or RE-M-BASO) and H-BASO (or RE-H-BASO) agree well with monoclinic phase of $BaAl_2Si_2O_8$ (JCPDS 38-1450) and the hexagonal phase of $BaAl_2Si_2O_8$ (JCPDS 28-0124), respectively. According to Lin and Forster's reports about polymorphism, there are four polymorphs of BASO (viz., hexagonal, monoclinic, paracelsian and orthorhombic [32,45]. Among existed polymorphs of BASO, we can synthesize both monoclinic and hexagonal BASO by changing the firing temperature, which also can be synthesized by solid state method [32]. In addition, the refined crystallographic unit cell parameters of the calcined products were calculated using the software Jade 5.0 and listed in Table 1.

### 4.2. Photoluminescence properties

The best way that detects the existence of $Sm^{2+}$ or $Sm^{3+}$ in one host lattice is to measure their PL emission process, and sometimes even if very small amount of Sm ions doped in one sample can be found through its characteristic PL spectra [46]. So PL properties can provides direct evidence for the reduction of $Sm^{3+}\rightarrow Sm^{2+}$.

The PL properties of $Sm^{3+}$ and $Sm^{2+}$ in different host lattices are quite different because of their different luminescent mechanism. $Sm^{2+}$ has the $4f^6$ electron configuration, and the $Sm^{2+}$ can be excited with UV to blue region and even the light extending over the full visible range [6,7,9,47,48], from which the ions rapidly relax to the lowest excited state. Just as the $Eu^{2+}$ or $Ce^{3+}$ ions, the luminescence wavelength of phosphors employing $Sm^{2+}$ changes greatly with the type of the host crystal [49–53]. However, generally, The emission lines of $Sm^{3+}$ are located at about 566, 604 and 649 nm, which are assigned to the ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$, ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$, ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$, respectively [54–57]. Their positions of f-f transitions coming from $Sm^{3+}$ change a little in different crystal sites.

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