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Synthesis, characterization of rare earth-alkaline earth oxide compounds

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Abstract

In this study, MR_2O_4 ($M = Ca, Sr, Ba$ and $R = Yb, Y, Dy, Eu, Sm$) with orthorhombic structure and $MRAIO_4$ ($M = Ca, Sr, Ba$ and $R = Yb, Y, Dy, Eu, Sm, Nd, La$) with tetragonal structure were prepared using sol gel based Pechini method. The influence of ionic radii of alkaline earth and rare earth elements on the stability of the phases in each synthesis series is discussed. The phase composition of the obtained powders was established by PXRD, the morphology by SEM. Furthermore the hydraulic behaviour of $SrEu_2O_4$, $SrAl_2O_4$ and $SrEuAlO_4$ were studied by isoperibolic calorimetry.

Keywords: Sol Gel Method; Alkaline Earth Rare Earth Oxides; XRD; SEM; Isoperibolic Calorimetry

1. Introduction

Crystalline compounds with the form MR_2O_4 ($M = Ca, Sr, Ba$ and $R =$ Rare Earth Element), often referred to as the $CaFe_2O_4$ structure type, are becoming increasingly important in the field of materials science due to their potential to be used as high temperature ceramic super conductors, superfine phosphors when doped with REE and electrode/electrolyte in solid oxide fuel cells (SOFCs) (Pöllmann et al., 2014; Bednorz et al., 1986; Zhou et al., 2005; Minh et al., 1993).

In the past, MR_2O_4 ($M = Ca, Sr, Ba$ and $R =$ Rare Earth Element) were mostly synthesised by high temperature solid-state methods, which require quite long reaction times at high temperatures. In recent years the sol gel based Pechini method has displayed advantages of lower synthesis temperatures, shorter synthesis times and considerably smaller resulting particle size. It employs complexing of cations using α -hydroxycarboxylic

acid such as citric acid in an aqueous-organic medium and makes use of low cost precursors resulting in a homogenous ion distribution at the molecular level (Huizar-Felix et al., 2012).

The present studies aim is to describe the synthesis of $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) system. The results of x-ray diffraction indicate that only samples with $x = 0, 1, 2$ consist of one single phase. Using the isoperibolic heat flow calorimetry the contrasting hydration behaviour of the monophasic phases are investigated. To study the role of ionic size of the alkaline earth and rare earth on the stability of rare earth alkaline earth oxides a series of MR_2O_4 ($M = \text{Ca, Sr, Ba}$ and $R = \text{R} = \text{Yb, Y, Dy, Eu, Sm}$) and MRAIO_4 ($M = \text{Ca, Sr, Ba}$ and $R = \text{Yb, Y, Dy, Eu, Sm, Nd, La}$) were synthesised using the Pechini method.

2. Experimental

2.1 Preparation of $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) system

The powder samples of $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) system were synthesized using the sol gel based Pechini method. The stoichiometric amounts of analytical grade $\text{Sr}(\text{NO}_3)_2$ was dissolved in distilled water and Eu_2O_3 was added into the aqueous solution as a nitric acid solution. Solid citric acid (4 moles citric acid per 1 mole earth alkaline) was added to the solution by stirring at 60 °C. After the ethylene glycol acid (7 moles ethylene glycol acid per 1 mole earth alkaline) was added, the solution was slowly evaporated at 100 °C to obtain a gel. The gel subsequently was dried at 130 °C in a drying cabinet overnight. The residue was ground in an agate mortar. Finally, the fine powders were annealed at 1300 °C for 4 hours in air.

2.2 Preparation of MR_2O_4 ($M = \text{Ca, Sr, Ba}$ and $R = \text{Yb, Y, Dy, Eu, Sm, Nd, La}$)

Analytical grade R_2O_3 ($R = \text{Yb, Y, Dy, Eu, Sm, Nd, La}$), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Ba}(\text{NO}_3)_2$ were used as starting materials. The gel was obtained as described in section 2.1. The dried gel was ground in an agate mortar. The annealing temperature was between 1000 – 1500 °C for 4 to 6 hours in air.

2.3 Characterization

Powder X-ray diffraction (PXRD) was performed using a PANalytical X'PERT Pro diffractometer system equipped with an X'celerator RTMS detector in Bragg-Brentano-geometry using Cu-K α -radiation. Silicon was used as internal standard at a level of 20% by mass. All phases were refined using the High Score Plus software from PANalytical. Structural images were obtained using VESTA and published atomic coordinates. SEM images were collected using a scanning electron microscope JSM 6300 (JEOL). The hydration behaviour of the phases was analysed by isoperibolic heat flow calorimetry.

3. Results and discussion

3.1 $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) system

Figure 1 depicts the X-ray diffraction pattern at room temperature for $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$). Only samples with $x = 0, 1, 2$ consist of one single phase. The first component SrAl_2O_4 shows different modification depending on temperature: the

compound SrAl_2O_4 changes from $\text{P}2_1$ to $\text{P}6_3$, and at temperatures above $1000\text{ }^\circ\text{C}$ into $\text{P}6_322$, as reported by Avdeev et al. (2007). However, the Pechini synthesized SrAl_2O_4 crystallises monoclinic low temperature modification. The second component SrEu_2O_4 belongs to the orthorhombic space group $\text{P}nam$ (62). Each europium atom is six-fold coordinated by oxygen anions, forming EuO_6 octahedra: the strontium atoms reside in honeycomb tunnels as one dimensional chain (Karunadasa et al., 2005). The intermediate phase SrEuAlO_4 belongs to the tetragonal space group $\text{I}4/mmm$. There are two types of cation sites in SrEuAlO_4 . The Sr^{2+} and Eu^{3+} ions are distributed in the nine-coordinated sites and the Al^{3+} ions occupy the six-coordinate site.

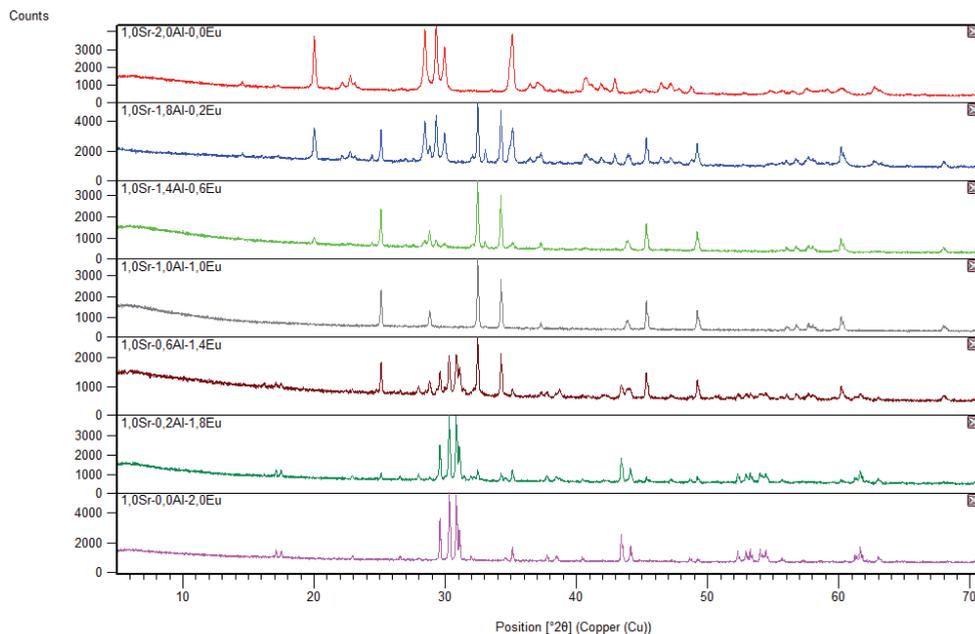


Fig. 1. X-ray diffraction patterns of $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ ($x = 0,2; 0,6; 1,0; 1,4; 1,8; 2,0$)

By varying the stoichiometric Sr/Eu ratio different compositions of $\text{SrEu}_x\text{Al}_{2-x}\text{O}_4$ were synthesized. Starting from SrAl_2O_4 , with increasing x the amount of SrAl_2O_4 decreased, at the same time the amount of SrEuAlO_4 increased until at $x = 1$ only SrEuAlO_4 could be detected. The further increasing x caused a decrease of SrEuAlO_4 and increased the amount of SrEu_2O_4 . At $x = 2$ only SrEu_2O_4 could be detected. The ionic size of strontium and europium are very similar but due to different oxidation states it is not possible to substitute strontium by europium without a change of the crystal structure.

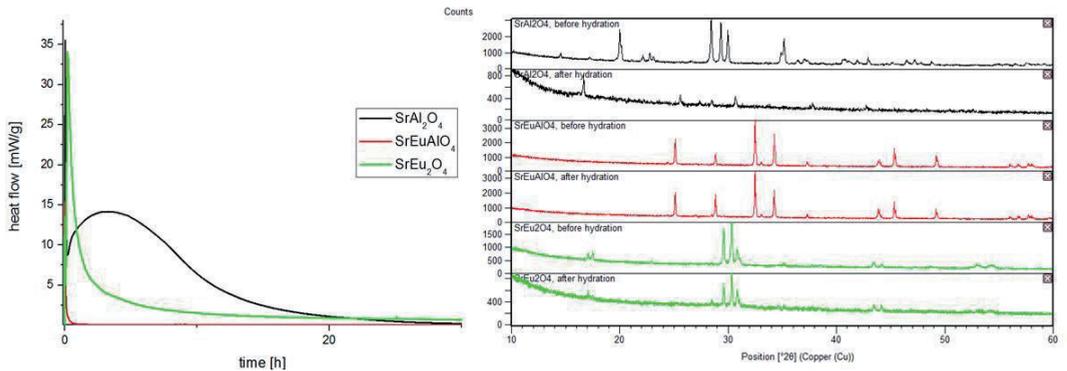


Fig. 2. a) Isoperibolic heat flow calorimetry of SrAl₂O₄, SrEuAlO₄ and SrEu₂O₄, water/solid-ratio: 1. b) Diffraction patterns of SrAl₂O₄, SrEuAlO₄ and SrEu₂O₄ before/after calorimetry

The results of the investigation of hydraulic behaviour of components and intermediate phase of the system SrEu_{2-x}Al_xO₄ with isoperibolic calorimetry are shown in Figure 2. The cement phase SrAl₂O₄ immediately reacts with water, forming SrAl-garnet and amorphous phase at 20 °C. No heat flow was detected with the intermediate phase SrEuAlO₄. The diffraction patterns before and after hydration showed no difference, hence SrEuAlO₄ does not seem to react with water. The REE component SrEu₂O₄ reacts with water forming an amorphous phase (Fig. 3).

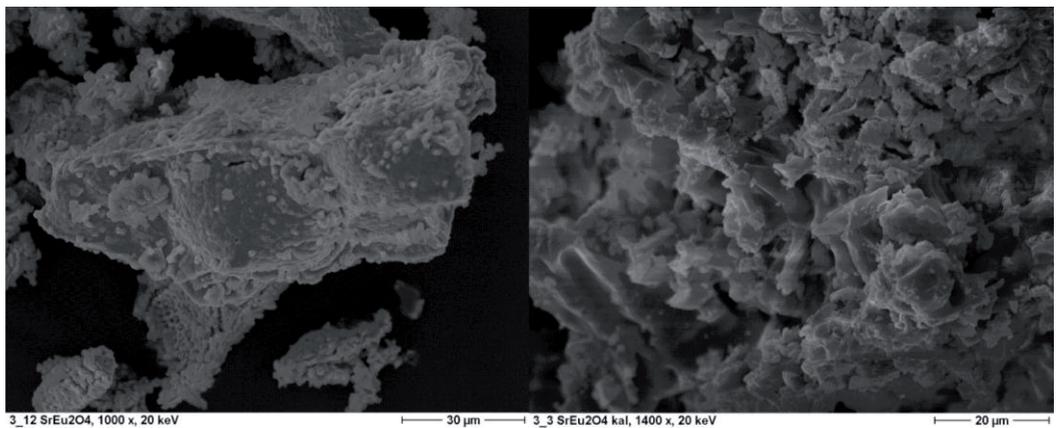


Fig. 3. SEM image of SrEu₂O₄ a) before hydration b) after hydration

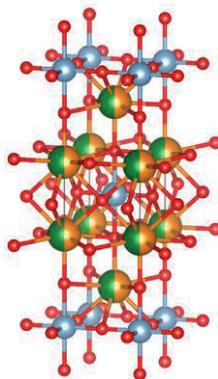
3.2 REE-phases isotypic to SrEu₂O₄

The substitution of europium by different rare earth elements and the substitution of strontium by calcium and barium were studied. The stability of the compounds depends highly on the ionic size of alkaline earth and rare earth elements. The ionic sizes of the discussed elements are given in Table 1.

Table 1. Ionic radii of selected elements (Data from Shannon et al. 1969)

Cations	Radii [pm]
Yb ³⁺	86
Y ³⁺	90
Dy ³⁺	91
Tb ³⁺	92
Eu ³⁺	95
Sm ³⁺	96
Ca ²⁺	100
Nd ³⁺	100
La ³⁺	106
Sr ²⁺	118
Ba ²⁺	135

The attempt to substitute europium by ytterbium, yttrium, dysprosium and samarium was successful: monophasic SrYb₂O₄, SrY₂O₄, SrDy₂O₄ and SrSm₂O₄ were synthesized. The substitution of strontium by barium, which has a significantly larger ionic radius than strontium, was also successful, leading to monophasic BaYb₂O₄, BaY₂O₄, BaDy₂O₄, BaEu₂O₄ and BaSm₂O₄. However, the substitution of strontium ions with much smaller calcium ions was not successful, the synthesis always led to starting oxides. The solid state synthesis of CaY₂O₄ and CaYb₂O₄ however, were reported by Barry et al. (1967), and Erfan et al. (2015). The calcium ion possibly is so small that it can only be stabilized in the RO₆ octahedra if ionic radii of R is smaller than 90 pm.

Fig. 4. Crystal structure of SrEuAlO₄ (green = Eu, orange = Sr, blue = Al, red = O)

3.3 Phases isotypic to SrEuAlO₄

The tetragonal structure of strontium europium aluminate is shown in Figure 4. Strontium and europium atoms are statistically distributed over the sites of the C_{4v} symmetry. For this phase to be stable the similar ionic radii of strontium and europium are essential. This was proved when the attempt to substitute europium by ytterbium, yttrium and dysprosium, which have much smaller ionic radii compared to strontium, failed. The

substitution of europium by samarium, neodymium and lanthanum led to monophasic SrSmAlO_4 , SrNdAlO_4 and SrLaAlO_4 .

The substitution of strontium by calcium, which has a similar ionic radius to rare earth elements, led to monophasic CaYbAlO_4 , CaYAlO_4 , CaDyAlO_4 , CaEuAlO_4 , CaSmAlO_4 , CaNdAlO_4 and CaLaAlO_4 . As expected the substitution of calcium by barium, which is bigger than rare earth elements was only possible with lanthanum, which has the biggest ionic radius among the rare earth elements. BaLaAlO_4 is not tetragonal, it possesses an orthorhombic structure similar to K_2SO_4 in space group $\text{P}2_12_12_1$ (Xiao 2007).

4. Conclusion

The present study demonstrates the synthesis of monophasic MR_2O_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{R} = \text{Yb}, \text{Y}, \text{Dy}, \text{Eu}, \text{Sm}$) and MRAIO_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ and $\text{R} = \text{Yb}, \text{Y}, \text{Dy}, \text{Eu}, \text{Sm}, \text{Nd}, \text{La}$) using the sol gel based Pechini method. In case of MR_2O_4 the ionic size of RO_6 octahedra in the orthorhombic structure is substantial for stabilizing alkaline earth metals in it: the small calcium ion can only be stabilized in YO_6 and YbO_6 octahedra. For tetragonal MRAIO_4 the similar ionic radii of alkaline earth and rare earth metals are critical, they share the same atom position.

The hydration behaviour of SrAl_2O_4 , SrEuAlO_4 and SrEu_2O_4 is quite different. While SrAl_2O_4 reacts with water immediately, SrEuAlO_4 does not react with water at all. SrEu_2O_4 partially reacts with water; a new amorphous phase is formed.

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