Synthesis, Characterization of compounds of earth alkaline rare-earth aluminates

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Introduction

Lasers based on ABAO₃ systems (A = Ca, Sr, Ba and B = REE) are promising materials for optical, electronic and structural applications. Yb-doped CaGdAlO₃ is well known for its smoothest emission spectrum (from 990 to 1080 nm) and a relatively high thermal conductivity. The poster reports on the sol gel preparation of ABAO₃ (A = Ca, Sr and B = Eu, Yb, Dy, Nd, Y und Sm). The synthesized compounds are studied by X-ray powder diffraction analysis and calorimetry.

Results

Monophasic CaBAlO₃ (B = Eu, Yb, Dy, Nd, Y und Sm) and SrBAlO₃ (B = Eu, Sm and Nd) are successfully synthesized by Pechini method. The ABAO₃ compounds belong to the tetragonal space group I4/mmm. As shown in representative example of CaNdAlO₃ (Figure 1) earth alkaline and REE atoms are statistically distributed over the sites of Cs₅. The AlO₃ octahedra form a two-dimensional net by corner-shared oxygen atoms. These AlO₃ layers are separated by (A, B)O slabs with the rock salt structure. The A and B cations are 9-coordinated to oxygen within this structural unit.

Unit cell refinement from powder diffraction using Pawley Method are summarized in Table 1. The cell parameters of CaBAlO₃ are plotted against the ionic radii in Figure 2a: unit cell parameters vary systematically with the REE cation size. It is in average of 156.33(9) and 164.90(4), as smaller cations (CaYb) are replaced by larger cations (CaNd). Figure 3 shows a SEM image of CaEuAlO₃.

In case of SrBAlO₃, it was only possible to incorporate Eu, Sm and Nd in strontium aluminates (Al : REE = 1:1) and not Yb, Y and Dy due to big difference in ionic radii between Sr and Yb (resp. Y and Dy). As seen in Figure 2b the unit cell volume increases with ionic radii of incorporated REE.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a [Å]</th>
<th>c [Å]</th>
<th>V [Å³]</th>
</tr>
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<tbody>
<tr>
<td>CaEuAlO₃</td>
<td>3.6461(6)</td>
<td>11.7597(4)</td>
<td>156.33(9)</td>
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<td>CaYbAlO₃</td>
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<td>11.8703(4)</td>
<td>157.49(9)</td>
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<td>CaDyAlO₃</td>
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<td>11.9122(2)</td>
<td>158.26(3)</td>
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<tr>
<td>CaNdAlO₃</td>
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<td>12.0156(4)</td>
<td>161.20(6)</td>
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<td>CaYbAlO₃</td>
<td>3.6696(6)</td>
<td>12.0598(8)</td>
<td>162.40(3)</td>
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<tr>
<td>CaSmAlO₃</td>
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<td>12.1458(2)</td>
<td>164.90(4)</td>
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<tr>
<td>SrEuAlO₃</td>
<td>3.7033(4)</td>
<td>12.3897(5)</td>
<td>169.92(2)</td>
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<tr>
<td>SrYbAlO₃</td>
<td>3.7110(1)</td>
<td>12.4238(2)</td>
<td>171.09(5)</td>
</tr>
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</table>

Table 1: Unit cell parameters, determined by X-ray powder diffraction at room temperature.

Methods

Monophasic earth alkaline rare-earth aluminates are synthesized by Pechini method. The gels were prepared using stoichiometric amounts of following chemicals:
- earth alkaline source: Ca(NO₃)₂, 4H₂O, Sr(NO₃)₂
- REE source: Yb(NO₃)₃·5H₂O, Dy₂O₃, Nd(NO₃)₃·6H₂O, Sm₂O₃, Eu₂O₃, Y(NO₃)₃·6H₂O
- Al source: Al(NO₃)₃·9H₂O

Nitrate solutions were dissolved in distilled water and oxides were added into the aqueous solution as a nitric acid solution. Solid citric acid (4 mole citric acid per 1 mole earth alkaline) was mixed to the solution by stirring at 80 °C. After the ethylene glycol acid (7 mole ethylene glycol acid per 1 mole earth alkaline) was added, solution was slowly evaporated at 100 °C to obtain a gel. The gel was further dried at 130 °C in a drying cabinet overnight. The residue was ground in an agate mortar. Finally, the fine powders were annealed at 1000 - 1500 °C in air.

X-ray powder diffraction (XRD) patterns were collected at room temperature between 10 and 70 (in 20) with PANalytical Xpert² Powder (CuKα1 radiation). The hydration behavior of the cements were analyzed by isoperibolic heat flow calorimetry.

Summary

The present study demonstrates the versatility of the Pechini method to yield monophasic compounds of earth alkaline rare-earth aluminates at low sintering temperature (1300 °C, 2h) when compared to the temperature required for solid state synthesis (>1400 – 1600 °C, over 48 h).

Monophasic CaBAlO₃ (B = Eu, Yb, Dy, Nd, Y und Sm) and SrBAlO₃ (B = Eu, Sm and Nd) are synthesized successfully and unit cell parameters are refined using Pawley method. The increase of unit cell volume in Ca and Sr series are in accordance with the ionic radii of REE, incorporated in aluminates.

References