X-ray Investigations of solid Solutions of Monocalcium Aluminate and Monostrontium Aluminate Important Phases in Cement and Phosphorescence Materials

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ABSTRACT
Calcium monoaluminate is the main phase in calcium aluminate cements and participates in the hydration, forming calcium aluminate hydrates. The amount of incorporation of foreign ions influences the hydration behaviour. Strontium aluminate is an important phase in producing phosphorescent materials when doped with REE as like Eu, Dy, La. These monoaluminates occur in different modifications. Monocalcium aluminate forms a monoclinic and an orthorhombic modification, whereas monostrontium aluminate forms a monoclinic low temperature and a hexagonal high temperature form.
Monoclinic monocalcium aluminate and monoclinic strontium aluminate form a partial solid solution series. Also the hydration behaviour of the different solid solutions was investigated using calorimetry. The newly formed strontium aluminate hydrates could be identified and similar strontium aluminate hydrates are formed. Solid solutions of strontium- and calcium-aluminate hydrates will be investigated.

INTRODUCTION
The components of the system and their structures are described by several authors (table 1). Both components form different modifications. CaAl$_2$O$_4$ crystallizes in a monoclinic space group P2$_1$/n (Dougill, M. W. 1957, Hörkner & Müller-Buschbaum 1975), confirmed by several authors. A metastable orthorhombic modification was synthesized by Raab et al. (2010) by low temperature synthesis method. SrAl$_2$O$_4$ crystallizes in monoclinic P2$_1$ or P2$_1$/n at room temperature and transforms into a hexagonal high temperature modification (P6$_3$) at about 650°C. Avdeev et al. described a high temperature phase in space group P 6$_3$22 at temperatures above 1273 K. Some selected crystallographic data for monocalcium aluminate and monostrontium aluminate are summarized in table 1.
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<th>Compound</th>
<th>Space group</th>
<th>a₀</th>
<th>b₀</th>
<th>c₀</th>
<th>β</th>
<th>Author</th>
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<td>CaAl₂O₄</td>
<td>P2₁/n</td>
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<td>Raab &amp; Pöllmann</td>
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<td>SrAl₂O₄</td>
<td>P₂₁</td>
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<td>SrAl₂O₄ (1073K)</td>
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<td>8.498</td>
<td>------</td>
<td>Fukuda et al.</td>
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<td>SrAl₂O₄ (1273K)</td>
<td>P6₃22</td>
<td>5.166</td>
<td>------</td>
<td>8.5485</td>
<td>------</td>
<td>Avdeev et al.</td>
</tr>
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</table>

Tab. 1 : Crystallographic data of CaAl₂O₄ and SrAl₂O₄

Solid solution studies in the system CaAl₂O₄ and SrAl₂O₄ have been already investigated by several authors. A complete solution series was described by Massazza et al. (1959), but limited solid solution series were described by Ito et al. (1977, 1979), Kuroki et al. (2009) and Prodjosanto et al. (2003) using XRD and synchrotron powder data.

**EXPERIMENTAL**

All phases were synthesized via the Pechini method with final temperature steps between 700 °C and 1200 °C for 1 hour. Powder X-ray diffraction (PXRD) was performed using a Panalytical X’Pert Pro diffractometer system equipped with X’celerator RTMS detector in Bragg-Brentano-geometry using Cu-Kα-radiation. Silicon was used as internal standard. All phases were refined using High Score Plus and Topas software. For temperature dependent XRD an Anton Paar HTK-16 heating chamber with platinum strip was applied. Structural images were obtained using ATOMS-program (DOWTY) and published atomic coordinates. SEM images were collected using scanning electron microscope JSM 6300 (JOEL). High resolution images of the microstructure were recorded with a LEO 1525 Gemini field emission scanning electron microscope equipped with a High-Efficiency InLens detector.

**RESULTS**

1. **Synthesis of Monostrontium aluminate**

Pure monostrontium aluminate was synthesised via the Pechini method at different final temperature steps between 700 °C and 1200 °C. Whereas no significant crystallinity was observed at 700 °C, at increasing temperature the crystallinity is improved owing to the crystallite growth as indicated by the sharpening of the reflections in PXRD pattern (Fig. 1).
Fig. 1: Improved crystallinity of SrAl$_2$O$_4$ synthesised via Pechini Method at different final temperature steps

Depending on the temperature the modification SrAl$_2$O$_4$ changes from P$_{2_1}$ to P$_{6_3}$ and for temperatures above 1000 °C into P$_{6_3}22$ as reported by Avdeev et al. 2007. In PXRD both polymorphs can be clearly distinguished owing to their specific reflection pattern, as demonstrated in figure 2.

Fig. 2: Comparison of simulated PXRD pattern of the different SrAl$_2$O$_4$ modifications: P$_{2_1}$ (bottom), P$_{6_3}$ (middle), P$_{6_3}22$ (top), intensity scale is in square roots.
However, whatever the final temperature the synthesised SrAl₂O₄ always possessed the monoclinic low temperature modification after rapid cooling down. Even in the PXRD pattern of the sample produced at 1200 °C no additional reflection of a hexagonal high temperature form are present (Fig. 3). The crystallised material shows a thin platy morphology, as presented in figure 4.

Fig. 3: PXRD pattern of monoclinic low temperature modification of SrAl₂O₄ synthesised via Pechini method with final temperature step at 1200 °C. (red: measurement, blue: LeBail fit, green: reflections).

Fig. 4: SEM micrograph of pseudohexagonal platelets of SrAl₂O₄.
2. Synthesis of solid solution series between CaAl$_2$O$_4$ and SrAl$_2$O$_4$

By varying the stoichiometric Sr/Ca ratio different compositions of Ca$_{1-x}$Sr$_x$Al$_2$O$_4$ were synthesized via Pechini method with a final temperature step at 1200 °C. The ionic radius of strontium being significantly larger than of calcium, the solid solution series is subdivided into 3 fields of different modifications that can be clearly distinguished by PXRD (Fig. 5). A substitution of Ca by Sr in the monoclinic CaAl$_2$O$_4$ (CA, SG P2$_1$/n) is possible up to 60 mole-%, i.e. Ca$_{0.4}$Sr$_{0.6}$Al$_2$O$_4$ without a change of the modification. Between 60 – 75 mole-% Ca substituted by Sr the modification of the synthesized compounds corresponds to the hexagonal high temperature polymorph of monostrontium aluminate (SG P6$_3$). Compositions with larger strontium contents, i.e. Ca$_{0.2}$Sr$_{0.8}$Al$_2$O$_4$ towards pure SrAl$_2$O$_4$ (SrA), crystallize in the monoclinic low temperature modification of monostrontium aluminate with SG P2$_1$.

Fig. 5: PXRD pattern of samples with different Ca/Sr ratios within the investigated solid solution series Ca$_{1-x}$Sr$_x$Al$_2$O$_4$ synthesized via Pechini method with final temperature step at 1200 °C. The modifications dependent on the composition are given in the right column.

The substitution of Ca by Sr in general leads to increased unit cell dimensions of the calcium-strontium aluminate compositions, shifting the strongest lines in PXRD pattern towards lower diffraction angles, as can be seen in figure 5. According to Avdeev et al. 2007 the phase transitions between the observed modifications are displacive, and thus the principle structural features are similar, except distortions of coordination polyhedron, deviation of certain atom positions and preferred occupations of the calcium positions. However, the unit cell set-ups are differently related to the principal structural features, as given in figure 6. Within the CA-type solid solution (Ca$_{1-x}$Sr$_x$Al$_2$O$_4$, 0 ≤ x ≤ 0.6, SG P2$_1$/n) the unit cell parameters systematically increase (Fig. 6). Increasing x(Sr) to 0.65 and changing the modification from CA-type (SG P2$_1$/n) into the high temperature SrA-type (SG P6$_3$), a
subsequent strong increase is observed for $c_0(P6_3)$, which structurally corresponds to $b_0(P2_1/n)$. The $a_0$ parameter, commonly designated for both modifications, is slightly lowered and is barely increased towards higher incorporation of Sr. A similar behavior is found comparing $a_0\sqrt{3}(P6_3)$ to $c_0(P2_1/n)$, bottom of figure 6. This value strongly increases when the modification is changed into the monoclinic low temperature form of SrA-type (SG P2$_1$) as the strontium concentration increases. The parameter $a_0(P2_1)$ follows the increasing tendency of $c_0(P6_3)$, whereas $b_0(P2_1)$ remains relatively constant.

Fig. 6: Unit cell parameters $a_0$, $b_0$, $c_0$ of different compositions Ca$_{1-x}$Sr$_x$Al$_2$O$_4$ corresponding to the observed modification (inset in the 3 different fields). Owing to the different unit cell set-ups the dimension of the parameters are adapted to comparable scales.

As a consequence of the increasing unit cell dimensions as the strontium concentration increases the unit cell volumes are enlarged, too. To enable comparability between the different unit cell set-ups of the observed modifications the specific volume per formula unit serves ($V_{\text{unit cell}}/Z$). As presented in figure 7, the specific volume depends by a distinct polynomial function on the stoichiometry: $V_{\text{spec}} = f(x)$. Whereas, $V_{\text{spec}}$ increasingly rises within the range of the CA-type solid solution, over the ranges of the hexagonal and the monoclinic SrA-type solid solutions the increase is diminished towards the pure SrAl$_2$O$_4$ (Fig. 7). Exceptionally the specific volume for the composition Ca$_{0.35}$Sr$_{0.65}$Al$_2$O$_4$ is lower than the functionally expected value and corresponds well with the turning point of the overall function at $x = 0.67$. Taking into account the unit cell parameters: $a_0(P6_3) < a_0(P2_1/n)$ and $c_0(P6_3, x=0.65)$ significantly lower than $c_0(P6_3, x=0.7)$, this composition obviously marks the stoichiometry related phase transition point. That result also corresponds to the finding of Prodjosantoso & Kennedy (2002) on the preferred site occupation of strontium on the calcium positions. However, in contrary to the phase mixtures at these Ca/Sr ration observed by
Prodjosantoso & Kennedy (2002, 2003), who used the solid state reaction synthesis, applying the Pechini method, pure single phases could be obtained.

As reported by Avdeev et al. 2007, the pure monoclinic SrAl$_2$O$_4$ undergoes polymorphic phase transitions towards temperatures increased over 1000°C: monoclinic P$\overline{2}_1$ → hexagonal P6$_3$ at about 680°C → P6$_3$22 at about 860°C. In order to prove the influence of the substitution of Sr by Ca in the monoclinic SrA-modification P$\overline{2}_1$ HT-XRD was carried out for the composition Ca$_{0.2}$Sr$_{0.8}$Al$_2$O$_4$ (Fig. 8). Therefore, the phase transition P$\overline{2}_1$ → P6$_3$ was found to be shifted towards an elevated temperatures and takes place in a range between 800°C and 850°C (Fig. 8).

Fig. 7: Specific volume ($V_{\text{unit cell}}/Z$) of solid solutions in the system CaAl$_2$O$_4$—SrAl$_2$O$_4$
SUMMARY AND CONCLUSION

Within the system monostrontium and monocalcium aluminate a replacement of calcium by strontium is possible resulting in a solid solution series. The exchange can be given by:

$$\text{Ca}_{(1-x)} \text{Sr}_{x} \text{Al}_2\text{O}_4$$

$$0 \leq x \leq 1$$

Three different regions of solid solutions can be distinguished, table 2. In the calcium-rich part the solid solutions are based on the monoclinic structure of monocalcium aluminate (SG P2\(_1\)/n), in the strontium-rich part the solid solutions are based on the monoclinic monostrontium aluminate (SG P2\(_1\)). A region in between strontium-rich (0.8-0.6 mole-%) and calcium-rich (0.4-0.2 mole-%) is based on the hexagonal high temperature modification of monostrontium aluminate (SG P\(_6_3\)). The monoclinic strontium-based solid solutions also undergo a transformation to a higher hexagonal symmetry at increasing temperature.
<table>
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<th>Symmetry</th>
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<td>\text{monoclinic}</td>
<td>\text{P 2}_1</td>
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Tab. 2: Symmetry within the solid solution series of \(\text{CaAl}_2\text{O}_4\) and \(\text{SrAl}_2\text{O}_4\).

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