TECHNICAL ARTICLE

X-ray investigations of solid solutions of monocalcium aluminate and monostrontium aluminate important phases in cement and phosphorescence materials

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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 rare-earth elements (REE) such as Eu, Dy, and La. These monoaluminates occur in different forms. Monocalcium aluminate forms a monoclinic and an orthorhombic modification, whereas monostrontium aluminate forms a monoclinic low-temperature and a hexagonal high-temperature form. Monoclinic calcium monoaluminate and monoclinic strontium aluminate form a partial solid-solution series. The hydration behaviour of different solid solutions was also investigated using calorimetry. The newly formed strontium aluminate hydrates could be identified while similar strontium aluminate hydrates are formed. Solid solutions of strontium- and calcium-aluminate hydrates will be investigated. © *2014 International Centre for Diffraction Data.* [doi:10.1017/S0885715614000189]

I. INTRODUCTION

Different investigations in the $Ca_{1-x}Sr_xAl_2O_4$ system are based on the importance of these phases as cement phases and also as long term phosphorescence materials (and also when doped with foreign elements) (Carlson (1955), Braniski (1957, 1965, 1967), Knopp (1962), Witzmann and Knopp (1963), Rodehorst *et al.* (2003), Ye *et al.* (2006), Saines and Kennedy (2006), Chatterjee (2009), Huang *et al.* (2009), Fu *et al.* (2010), Hwang *et al.* (2011), Mohr (2011), Pöllmann (2012)).

The components of the system and their structures are described by several authors (Table 1). Both components form different modifications. $CaAl_2O_4$ crystallizes in a monoclinic space group $P2_1/n$ (Dougill, (1957), Hörkner and Müller-Buschbaum (1975)), and confirmed by several authors. A metastable orthorhombic modification was synthesized by Raab and Pöllmann (2010) by a low-temperature synthesis method. $SrAl_2O_4$ 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.* (2007) described a high-temperature phase in the space group $P6_322$ at temperatures above 1273 K. Some selected crystallographic data for monocalcium aluminate and monostrontium aluminate are summarized in Table 1.

Solid-solution studies in the system $CaAl_2O_4$ and $SrAl_2O_4$ have been already investigated by several authors. A complete solution series was described by Massazza and Cannas (1959), but limited solid-solution series were described by Ito *et al.* (1977, 1979), Kuroki *et al.* (2009), and Prodjosanto *et al.* (2002, 2003) using X-ray diffraction (XRD) and synchrotron powder data.

II. EXPERIMENTAL

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

III. RESULTS

A. Synthesis of monostrontium aluminate

Pure monostrontium aluminate was synthesized via the Pechini method at different final temperature steps between 700 and 1200 °C. Whereas no significant crystallinity was observed at 700 °C, at increasing temperature the crystallinity improved as indicated by the sharpening of the reflections in the PXRD pattern (Figure 1).

Depending on the temperature the modification of $SrAl_2O_4$ changes from $P2_1$ to $P6_3$ and for temperatures above 1000 °C into $P6_322$ as reported by Avdeev *et al.* (2007). In PXRD, both polymorphs can be clearly

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TABLE I. Crystallographic data of $CaAl_2O_4$ and $SrAl_2O_4$.

Compound	Space group	a_0	b_0	c_0	ß	Reference
$CaAl_2O_4$	$P2_1/n$	8.7001	8.0943	15.2074	90.156	Prodjosanto et al. (2002)
$CaAl_2O_4$	Orthorhombic	8.737	8.076	15.12	–	Raab and Pöllmann (2010)
$CaAl_2O_4$	$P2_1/n$	8.700	8.092	15.19	90.19	Raab and Pöllmann (2010)
$SrAl_2O_4$	$P2_1$	8.447	8.816	5.163	93.42	Schulze and Müller-Buschbaum (1981)
$SrAl_2O_4$	$P2_1/n$	8.4402	8.8204	5.1557	93.41	Prodjosanto et al. (2002)
$SrAl_2O_4$ (1073 K)	$P6_3$	8.926	–	8.498	–	Fukuda and Fukushima (2005)
$SrAl_2O_4$ (1273 K)	$P6_322$	5.166	–	8.5485	–	Avdeev et al. (2007)

TABLE II. Symmetry within the solid-solution series of $CaAl_2O_4$ and $SrAl_2O_4$.

Composition	Symmetry	Space group	Phase transformation
$Ca_1 Sr_0 Al_2O_4$–$Ca_{0.4} Sr_{0.6} Al_2O_4$	Monoclinic	$P2_1/n$	No
$Ca_{0.4} Sr_{0.6} Al_2O_4$ $Ca_{0.2} Sr_{0.8} Al_2O_4$	Hexagonal	$P6_3$	No
$Ca_{0.2} Sr_{0.8} Al_2O_4$ $Ca_0 Sr_1 Al_2O_4$	Monoclinic	$P2_1$	Yes to the hexagonal HT-phase

distinguished owing to their specific reflection pattern, as demonstrated in Figure 2.

However, irrespective of the final temperature, the synthesized $SrAl_2O_4$ always possessed the monoclinic low-temperature modification after rapid cooling. Even in the PXRD pattern of the sample produced at 1200 °C, no reflections indicating a hexagonal high temperature form are present (Figure 3). The crystallized material shows a thin platy morphology, as presented in Figure 4.

B. Synthesis of solid-solution series between $CaAl_2O_4$ and $SrAl_2O_4$

By varying the stoichiometric Sr/Ca ratio, different compositions of $Ca_{1−x}Sr_xAl_2O_4$ were synthesized via the Pechini method with a final temperature step at 1200 °C. The ionic radius of strontium being significantly larger than that of calcium, the solid-solution series is subdivided into three fields of different modifications that can be clearly distinguished by PXRD (Figure 5). A substitution of Ca by Sr in the monoclinic $CaAl_2O_4$ (CA, SG $P2_1/n$) is possible up to 60 mole%, i.e. $Ca_{0.4}Sr_{0.6}Al_2O_4$ without a change of the modification. Between 60 and 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. $Ca_{0.2}Sr_{0.8}Al_2O_4$ towards pure $SrAl_2O_4$ (SrA), crystallize in the monoclinic low-temperature modification of monostrontium aluminate with SG $P2_1$.

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 the PXRD pattern towards the 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 principal structural features are similar, except for the distortions of coordination polyhedron, deviation of certain atom positions, and preferred occupations of the calcium positions. However, the unit-cell setups are differently related to the principal structural features, as given in Figure 6.

Within the CA-type solid solution ($Ca_{1−x}Sr_xAl_2O_4$, $0 \leq x \leq 0.6$, SG $P2_1/n$) the unit-cell parameters systematically increase (Figure 6). Increasing x(Sr) to 0.65 and changing the modification from CA-type (SG $P2_1/n$) into the high-
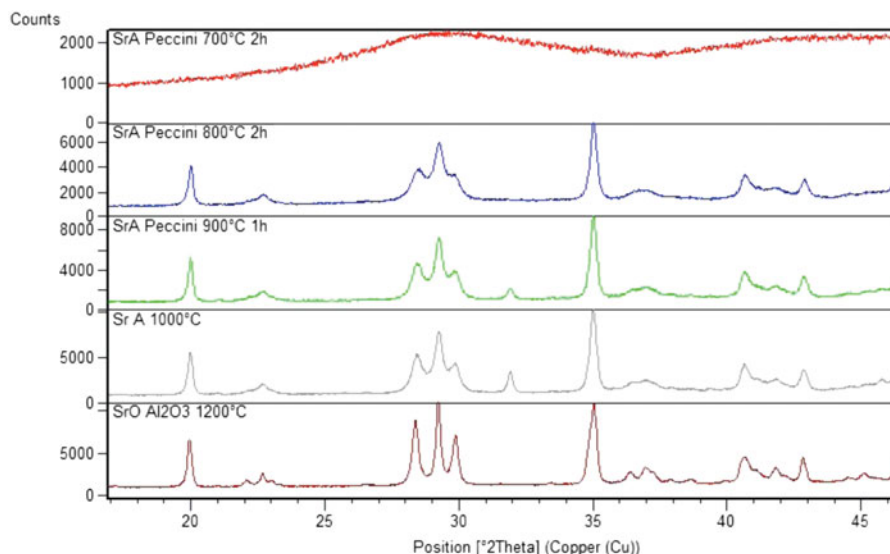
Figure 1. (Color online) Improved crystallinity of $SrAl_2O_4$ synthesized via Pechini Method at different final temperature steps.
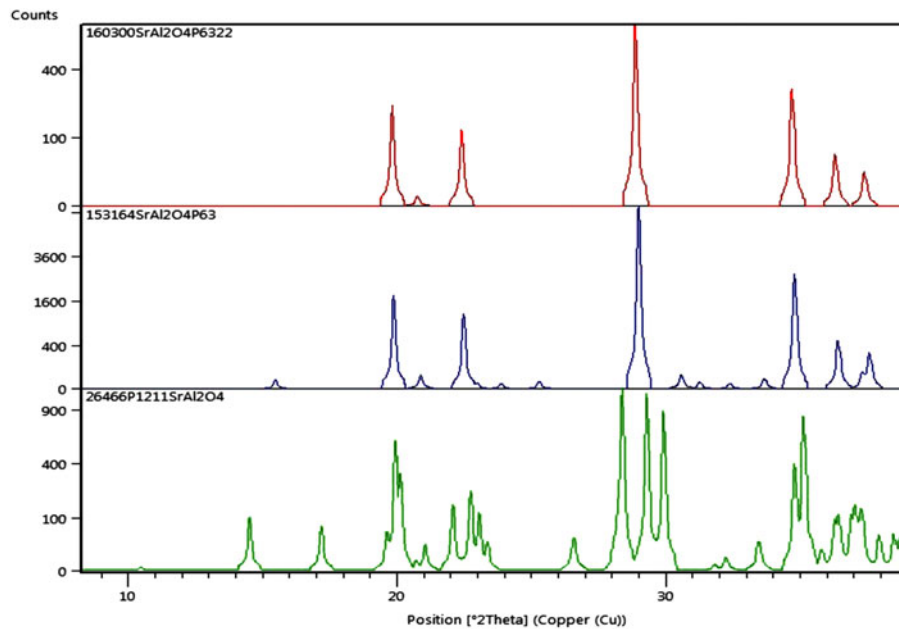
Figure 2. (Color online) Comparison of the simulated PXRD pattern of the different SrAl₂O₄ modifications: $P2_1$ (bottom), $P6_3$ (middle), and $P6_322$ (top).
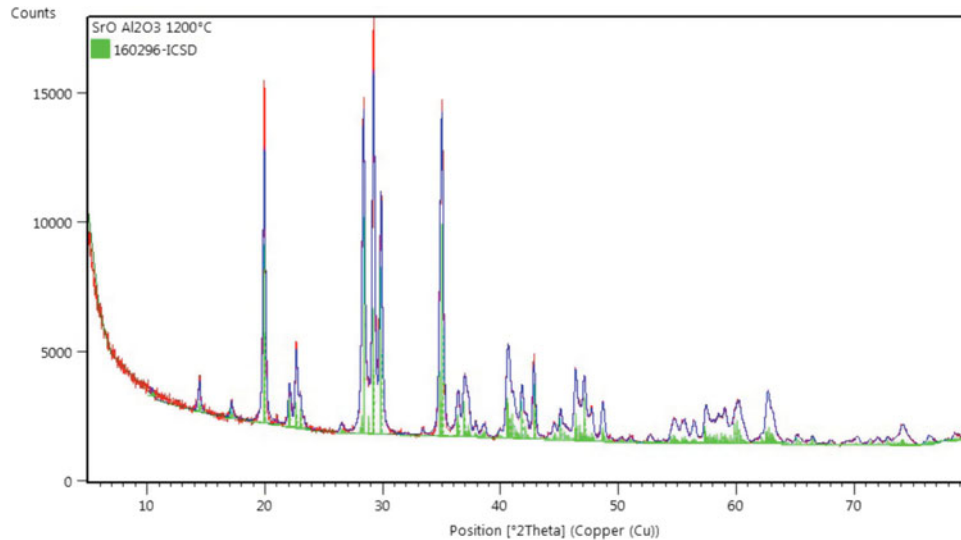

Figure 3. (Color online) PXRD pattern of monoclinic low-temperature modification of SrAl₂O₄ synthesized via the Pechini method with final temperature step at 1200 °C (red: measurement, blue: LeBail fit, green: reflections).
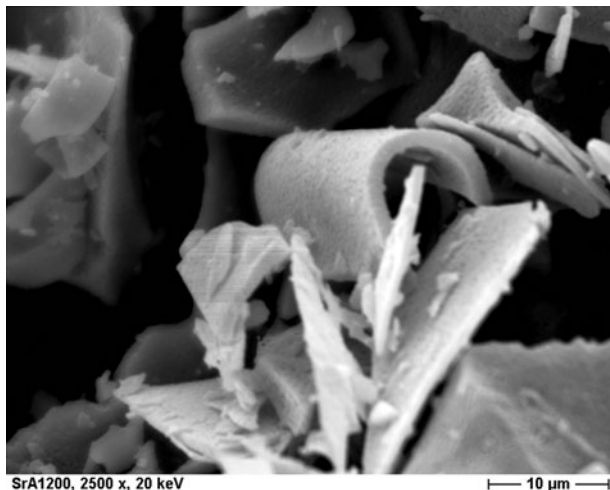

Figure 4. SEM micrograph of pseudohexagonal platelets of SrAl₂O₄.

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 behaviour 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 Sr 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.

As a consequence of the increasing unit-cell dimensions as the Sr concentration increases the unit-cell volumes are enlarged, too. To enable comparability between the different unit-cell setups of the observed modifications the specific volume per formula unit is ($V_{unit-cell}/Z$). As presented in Figure 7, the specific volume depends on a distinct polynomial
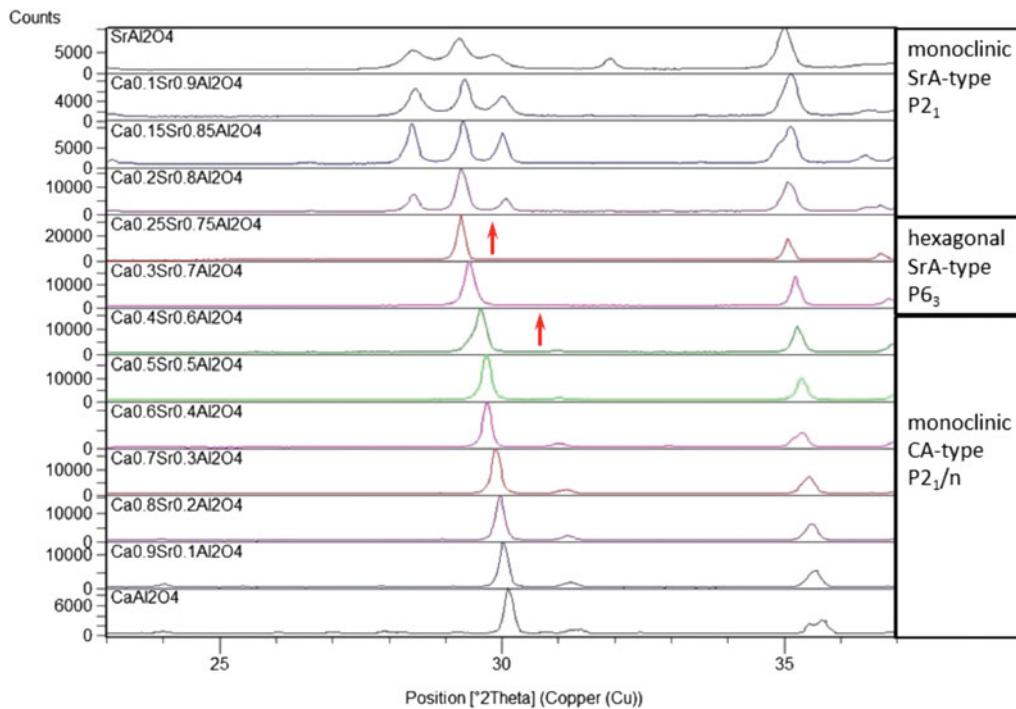
Figure 5. (Color online) PXRD pattern of samples with different Ca/Sr ratios within the investigated solid-solution series $Ca_{1-x}Sr_xAl_2O_4$ synthesized via the Pechini method with final temperature step at 1200 °C. The modifications dependent on the composition are given in the right column.

function on the stoichiometry: $V_{spec} = f(x)$. Whereas, V_{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 $SrAl_2O_4$ (Figure 7). Exceptionally the specific

volume for the composition $Ca_{0.35}Sr_{0.65}Al_2O_4$ 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 $c_0(P6_3, x = 0.65)$ are significantly lower than
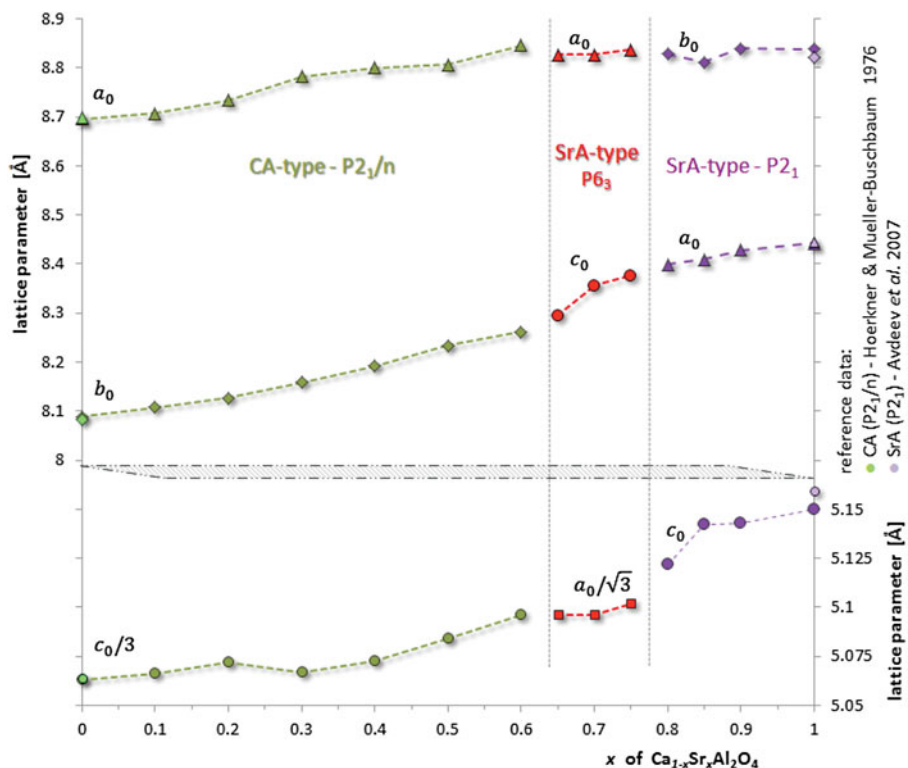

Figure 6. (Color online) Unit-cell parameters a_0, b_0, c_0 of different compositions $Ca_{1-x}Sr_xAl_2O_4$ corresponding to the observed modification (inset in the three different fields). Owing to the different unit-cell setups the dimension of the parameters are adapted to comparable scales.
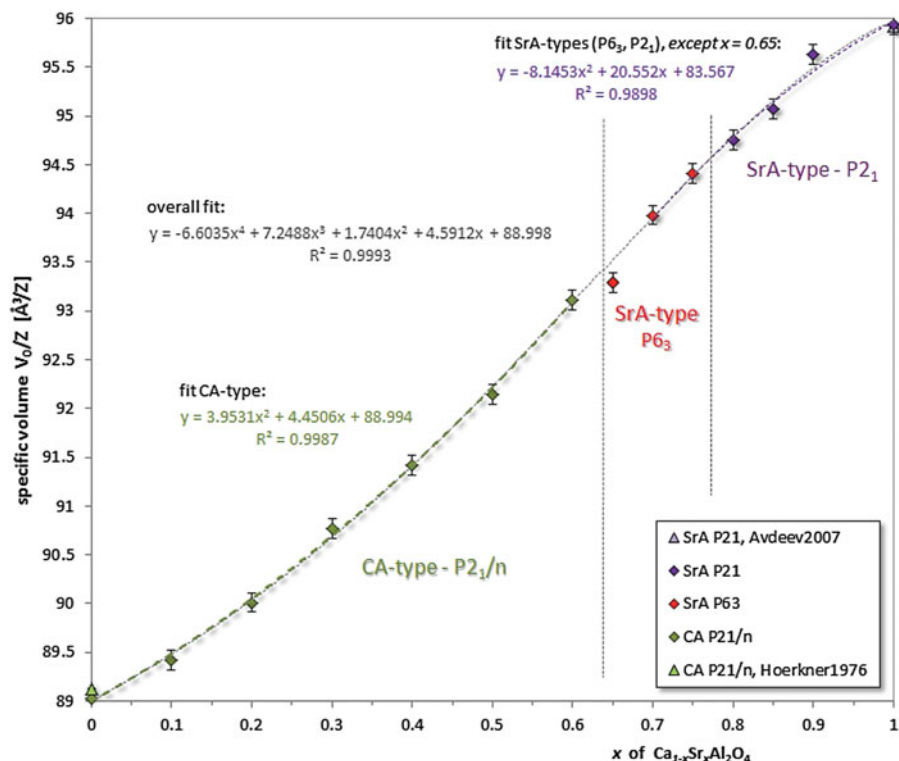
Figure 7. (Color online) Specific volume ($V_{unit\text{-}cell}/Z$) of solid solutions in the system $CaAl_2O_4$–$SrAl_2O_4$.

$c_0(P6_3, \ x = 0.7)$, this composition obviously marks the stoichiometry-related phase-transition point. The result also corresponds to the finding of Prodjosantoso and Kennedy (2002) on the preferred site occupation of strontium on the calcium positions. However, in contrary to the phase mixtures at these Ca/Sr ratio observed by Prodjosantoso and Kennedy

(2002, 2003), whose 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 $SrAl_2O_4$ undergoes polymorphic phase transitions when the temperature is increased over 1000 °C: monoclinic $P2_1 \rightarrow$
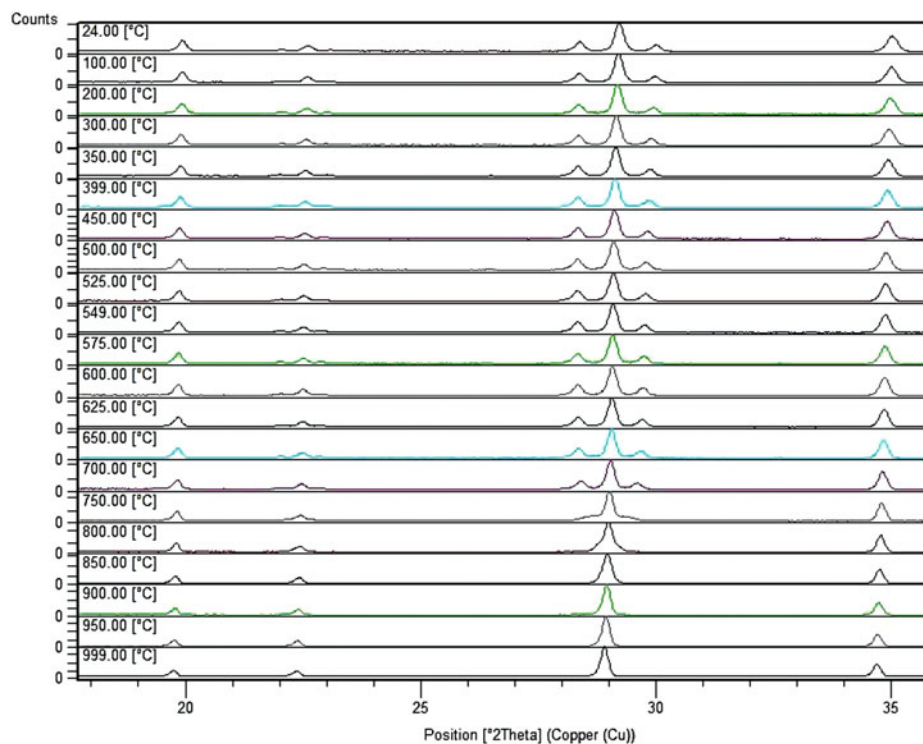

Figure 8. (Color online) HT-XRD measurement of $Ca_{0.2}Sr_{0.8}Al_2O_4$ between 25 and 1000 °C.

hexagonal $P6_3$ at about $680\,°C \rightarrow P6_322$ at about $860\,°C$. In order to prove the influence of the substitution of Sr by Ca in the monoclinic SrA-modification $P2_1$ high-temperature XRD (HT-XRD) was carried out for the composition $Ca_{0.2}Sr_{0.8}Al_2O_4$ (Figure 8). Therefore, the phase transition $P2_1 \rightarrow P6_3$ was found to be shifted towards an elevated temperature and takes place in a range between 800 and 850 °C (Figure 8).

IV. 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 as:

$$Ca_{(1-x)}\,Sr_{(x)}\,Al_2O_4$$
$$0 \leq x \leq 1$$
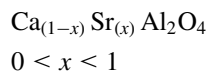
Three different regions of solid solutions can be distinguished. In the calcium-rich part the solid solutions are based on the monoclinic structure of monocalcium aluminate (SG $P2_1/n$), in the strontium-rich part the solid solutions are based on the monoclinic monostrontium-aluminate (SG $P2_1$). A 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 mono-strontium aluminate (SG $P6_3$). The monoclinic strontium-based solid solutions also undergo a transformation to a higher hexagonal symmetry at increasing temperature.

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