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Crystallisation of spray-dried amorphous precursors in the $SrO–Al_2O_3$ system: a DSC study

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Abstract

The crystallisation of amorphous precursors in the $SrO–Al_2O_3$ system has been studied by DSC and XRD. Amorphous precursors were obtained for compositions ranging from $12SrO.7Al_2O_3$ to Al_2O_3 by spray-drying aqueous solutions of strontium and aluminium nitrates followed by heating the powders to decompose the nitrates. Of the stable compounds SrA, SrA_2 and SrA_6, only SrA crystallises directly at a usual heating rate of 5 °C/min (in this notation Sr = SrO and $A = Al_2O_3$). All the alumina-richer compositions are characterised by the first and strong crystallisation of metastable solid solutions of SrA in its hexagonal form, stabilised by excess aluminium cations, or γ-Al_2O_3 stabilised by strontium cations, or even the two solid solutions, depending on the composition. The hexaaluminate SrA_6 is formed as single phase by an exothermic transformation of the γ-Al_2O_3 solid solution at 1183 °C. The formation of SrA_2 is complicated by the easy and competitive formation of Sr_4A_7, of close composition. The latter compound is stable only up to 1500 °C and is decomposed at higher temperatures. However SrA_2, which is characterised by a slow kinetics of formation from the amorphous state as well as from the high temperature liquid state, may be obtained pure by slow heating or annealing at 900–1000 °C.

Keywords: Crystallisation; Powders-chemical synthesis; Strontium aluminates; $SrAl_2O_4$; Phase development

1. Introduction

Despite large similarities with their closely related calcium counterparts, strontium aluminates have received much less interest. Beside their potential as refractory oxides in the steel industry and binder materials in the cement industry, they are of interest in materials science because of their use as long-duration photoluminescence or thermoluminescence pigments. Doped with rare-earth metal ions such as Eu^{2+} they exhibit excellent properties such as high quantum efficiency[1] and long persistence of phosphorescence.[2]

Compared with the better known $CaO–Al_2O_3$ system, the $SrO–Al_2O_3$ phase diagram (Fig. 1)[3] is slightly different and many uncertainties are still remaining, especially concerning the melting points and the melting behaviours of many compounds, or more basically the existence of some compounds. Sr_3A, SrA, SrA_2 and SrA_6 are stable double oxides, isostructural with C_3A, CA, CA_2 and CA_6 (in the cement chemistry notation C = CaO, Sr = SrO and $A = Al_2O_3$). Sr_4A has been described by Massazza[4] to be stable only above 1125 °C, under the β form between 1125° and 1320 °C or the α form between 1320 and 1690 °C. Sr_4A_7 was hydrothermally synthesised by Nadezhina et al.[5] This compound was more recently synthesised by solid-state chemistry by Minquan et al.[6] and Lin et al.[7] We confirmed the easy synthesis of this compound and its domain of stability, between ≈1100 and 1500 °C.[8] Yamaguchi[9] described a sol-gel synthesis of $Sr_{12}A_7$, homologous with $C_{12}A_7$, crystallising at 840–900 °C but decomposing at higher temperature into Sr_3A and SrA. Recently Kahlenberg[10] found single crystals of $Sr_{10}A_3$ on the surface of strontium-rich pellets sintered at 1600 °C for 144 h.

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In the course of our study of the local structure of high temperature SrO–Al_2O_3 liquids[11] we compared these liquids with amorphous and crystalline phases of same compositions. And therefore we made a systematic study of the crystallisation of the known compounds from amorphous precursors. The present paper reports this study. The amorphous precursors have been obtained from a simple process: spray-drying aqueous solutions of strontium and aluminium nitrates, followed by heat treatment. This process had revealed to be very efficient for the synthesis of chemically homogeneous amorphous powders in the CaO–Al_2O_3 system.[12]

2. Experimental procedure

A spray-drying and calcination process led to amorphous powders with the desired compositions. For this, mixtures of titrated aqueous solutions (0.5–1 M) of strontium and aluminium nitrates (Aldrich) were spray-dried using a laboratory apparatus (Büchi, Flawil, Switzerland, 190 mini spray-drier equipped with a 0.5 mm diameter nozzle). This atomiser operates on the principle of nozzle spraying in parallel flow, i.e. the sprayed product and the drying air flow in the same direction. The drying air was heated to 200–210 °C. One part of the collected powder was used for a thermogravimetric analysis (TGA) of the decomposition. The rest of the powder was heated in a ventilated furnace, at 5 °C/min, to 750 °C for 3 h, and the resulting amorphous powder, except for the strontium-rich compositions, was used for the study of the crystallisation. Thermal analysis data, for TGA and differential scanning calorimetry (DSC) were collected separately on Setaram apparatuses (Caluire, France) using a 5 °C/min heating rate under air atmosphere. DSC analyses were performed on 200–300 mg of powder and α-Al_2O_3 was used as a reference. X-ray diffraction (XRD) at room temperature (Cu-K_α radiation, Philips PW1729 diffractometer, Eindhoven, The Netherlands) was used to identify the different crystalline phases.

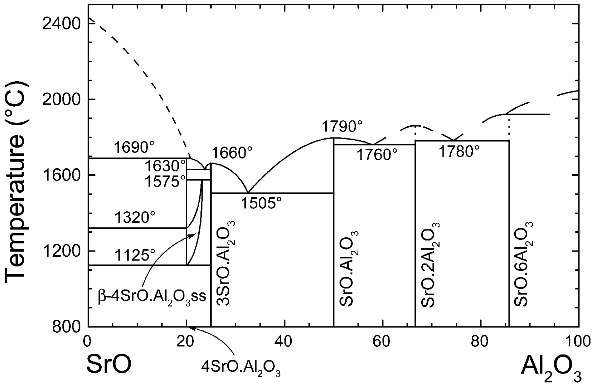

Fig. 1. SrO–Al_2O_3 diagram, after Massazza.[3]

3. Results and discussion

3.1. Synthesis

The process of synthesis used in this study is simple and rapid: spray-drying aqueous solutions, followed by heat-treatment in order to decompose the nitrate ions. This process has proved to be very efficient in the synthesis of chemically homogeneous powders precursors of alkaline earth aluminates[13] and especially calcium aluminates[12] and also silicates like magnesium silicates[14] and aluminosilicates like mullite[15,16] and cordierite.[17] The spray-drying process is well known in ceramic powder synthesis[18] and usually yields hollow spheres. Fig. 2 shows a typical micrograph for a SrA_2 precursor powder calcined at 750 °C. The particle size ranges from about 0.5 to 5 µm, as measured on the micrograph.

3.2. Thermogravimetric analysis

The decomposition of the nitrates has been studied by thermogravimetry. In Fig. 3 are reported the TGA

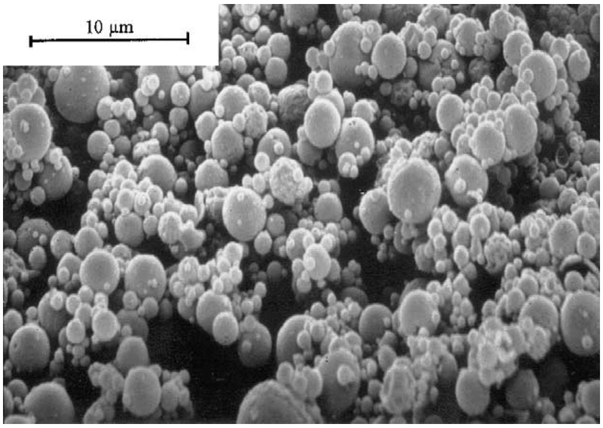

Fig. 2. Scanning electron micrograph of a spray-dried powder precursor of SrA_2 heated to 750 °C for 3 h.

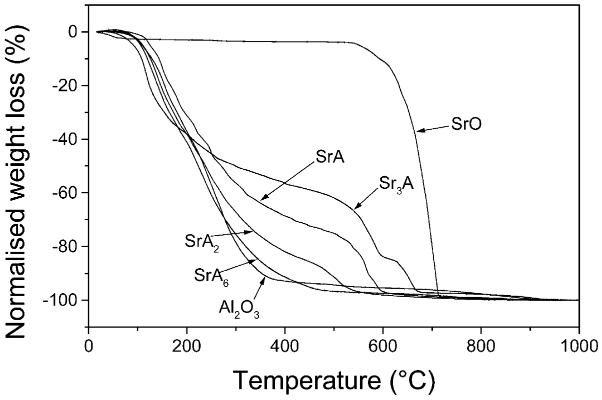

Fig. 3. TGA curves of the spray-dried powders of different compositions in the SrO–Al_2O_3 system; heating rate: 5 °C/min. The weight losses are normalised to 100% at 1000 °C for comparison.

curves of spray-dried powders of various compositions in the SrO–Al_2O_3 system. For comparison these curves have been scaled to 100% of the weight loss at 1000 °C for each composition. The spray-dried powder from aluminium nitrate is decomposed between 100 and 350 °C, with two maxima for the weight loss rate, determined from the derivative curve at 145 and 265 °C (not shown). When spray-dried, the aluminium nitrate is already partially decomposed, and its complete decomposition is achieved via an intermediate oxynitrate[12] at the difference of commercial aluminium nitrate nonahydrate that is decomposed through a single step at about 220 °C when treated at the same heating rate.

Strontium nitrate alone is decomposed between 535 and 720 °C with a sharp maximum at 703 °C in the rate of weight loss. As one can see in Fig. 3, it is clear that for the powders resulting from spray-drying mixtures of the two nitrates, the decomposition of strontium nitrate is shifted to lower temperatures as the aluminium content is increased; and the decomposition of aluminium nitrate is also influenced by the presence of strontium nitrate in the powder. This behaviour at the decomposition of the nitrates was also noted in the case of calcium aluminates.[12]

3.3. Crystallisation

Except for the strontium-rich compositions (Sr_3A and Sr_4A) the powders annealed at 750 °C for 3 h were amorphous and were suitable for the study of the crystallisation. The DSC curves, at a heating rate of 5°/min, of the amorphous precursors corresponding to the known stable phases and some other compositions in the SrO.Al_2O_3 system are reported in Figs. 4 and 5.

3.3.1. Al_2O_3 and SrA_6 ($SrAl_{12}O_{19}$)

The thermograms of Al_2O_3 and SrA_6 precursors exhibit each two exothermic peaks and have to be compared (Fig. 4). The spray-dried amorphous precursor of alumina crystallises into a highly disordered transition alumina phase (η- or γ-Al_2O_3) through a first exothermic peak at 845 °C and transforms into the stable α-Al_2O_3 phase through a second exotherm at 1142 °C. For the hexaaluminate composition, the two exothermic peaks are sharper and delayed to higher temperatures (936 and 1183 °C). For the sample just heated beyond the first peak, the XRD diagram displays only the broad and diffuse peaks characteristic of a badly crystallised transition alumina, probably γ-Al_2O_3 (Fig. 6). After the second exothermic peak only the SrA_6 magnetoplumbite phase can be observed. The second exotherm reflects the transformation of the γ-Al_2O_3 solid solution into the pure and well ordered hexa-aluminate.

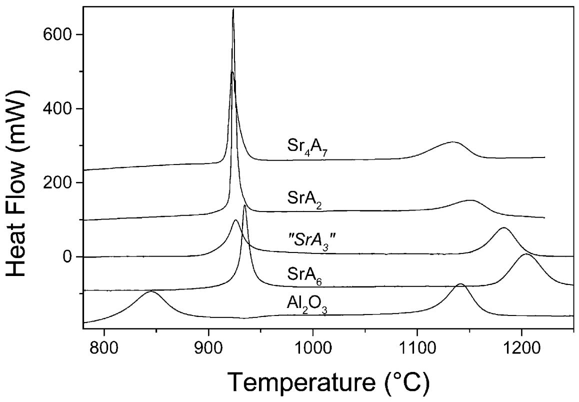

Fig. 4. DSC curves of the alumina-rich amorphous precursors; heating rate: 5 °C/min.

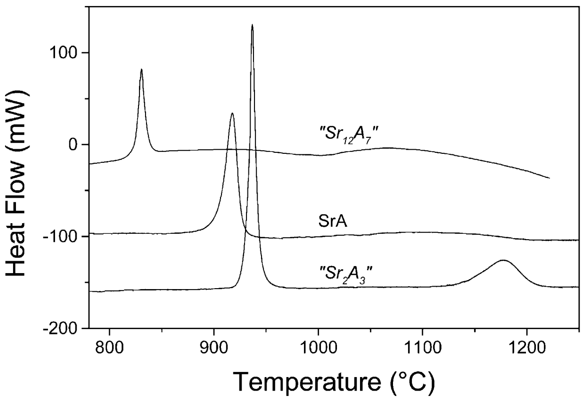

Fig. 5. DSC curves of amorphous precursors of SrA and two surrounding compositions; heating rate: 5 °C/min.

By this process of synthesis strontium ions can be easily incorporated into the defect spinel structure of the transition alumina. The γ-Al_2O_3 structure may be stabilised by replacing the Al^{3+} and vacancies in the tetrahedral sites by M^{2+} cations having ionic radii close to that of Al^{3+} (0.51 Å), giving a maximum structural stability for the stoichiometry MO.2Al_2O_3. In the case of Sr^{2+} the ionic (1.12 Å) radius is really too high and not compatible with a tetrahedral coordination. However a marked stabilising effect is observed for the SrO.6Al_2O_3 stoichiometry. Compared to the undoped

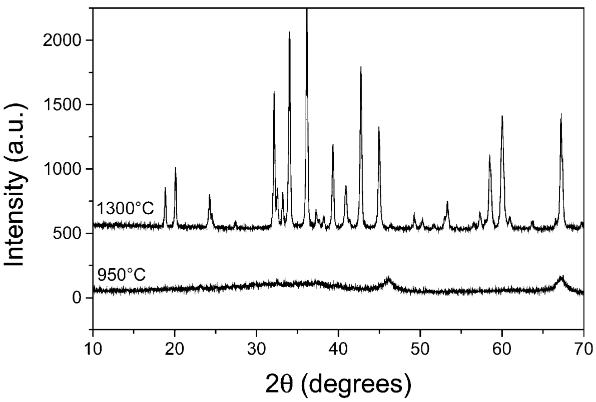

Fig. 6. XRD patterns of the SrA_6 precursor after heating to 950 °C (γ-Al_2O_3 solid solution) and 1300 °C (SrA_6 single phase).

alumina precursor, the presence of the strontium cations renders the ordering of the structure more difficult and needs higher temperatures for its formation. On the other hand higher temperatures are also needed for its transformation. This stabilising effect on the transition aluminas is also observed with calcium and barium ions.[12,13] The efficiency in the stabilising effect is in the order of increasing ionic radius: Ca < Sr < Ba (0.99, 1.12 and 1.34 Å respectively).

Like CA_6[12] SrA_6 is obtained easily and pure by this process of synthesis at relatively low temperature. Many works have been devoted to CA_6 and the chemical synthesis of this pure compound usually requires high temperatures with long durations of thermal treatment.[19] In the present study we show that SrA_6 is synthesised as easily as CA_6, corroborating the high efficiency of spray-drying nitrates solutions for the production of chemically very homogeneous precursors.

3.3.2. SrA ($SrAl_2O_4$)

SrA is a stable compound in the SrO–Al_2O_3 system. It crystallises through a single exothermic peak at 917 °C on DSC analysis (Fig. 5). The stable structure at ambient temperature is monoclinic (JCPDS file 34-0379). The crystallinity of the sample after the exothermic peak is just improved by annealing at higher temperature (Fig. 7). It is known that the monoclinic strontium monoaluminate SrA transforms at high temperature, at about 650 °C, into the hexagonal polymorph (JCPDS file 31-1336).[20] This has been checked by in-situ XRD study of the structural evolution with temperature,[8] and by DSC study of the crystallised sample (Fig. 8). The monoclinic-hexagonal transformation is endothermic ($\Delta H = 3.2$ kJ/mol) and the reverse hexagonal-monoclinic one is exothermic. The hexagonal polymorph can be easily stabilised at room temperature as solid solution with many cations like calcium, silicium or excess aluminium[8,21] as it is the case in the present study for a wide scale of compositions between $SrO.Al_2O_3$ and $SrO.6Al_2O_3$.

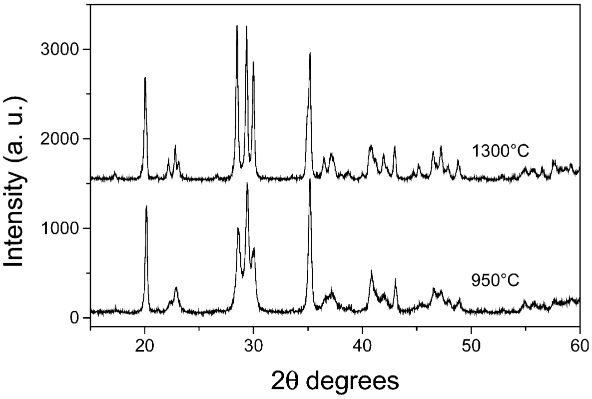

Fig. 7. XRD diagrams of the SrA precursor after heating to 950 and 1300 °C: monoclinic SrA single phase.

3.3.3. SrA_2 and Sr_4A_7 ($SrAl_4O_7$ and $Sr_4Al_{14}O_{25}$)

SrA_2 and Sr_4A_7 cannot be dissociated. Their compositions are close: 33.3 mol% SrO 66.7 mol% Al_2O_3 for SrA_2 and 36.4 mol% SrO 63.6 mol% Al_2O_3 for Sr_4A_7. The DSC curves, at 5 °C/min (Fig. 4) exhibit a first and sharp exothermic peak at 923 °C and a second and wider exotherm at 1135 °C for Sr_4A_7 and 1150 °C for SrA_2. After heating to 1000 °C in order to characterise the first exothermic peak by XRD identification, the sample of composition $4SrO.7Al_2O_3$ has crystallised into a mixture of two solid solutions: the hexagonal SrA stabilised by excess Al atoms and γ-Al_2O_3, stabilised by Sr atoms, the latter solid solution being more scarcely discernible on the XRD diagram (Fig. 9). The presence of this transition alumina solid solution has been confirmed by a detailed high resolution ^{27}Al MAS NMR spectroscopy study.[8,22] These two solid solutions combine at higher temperature (second exothermic peak) to yield pure Sr_4A_7. This compound is easily synthesised.

For the SrA_2 precursor, the same two solid solutions were found after the crystallisation, along with SrA_2

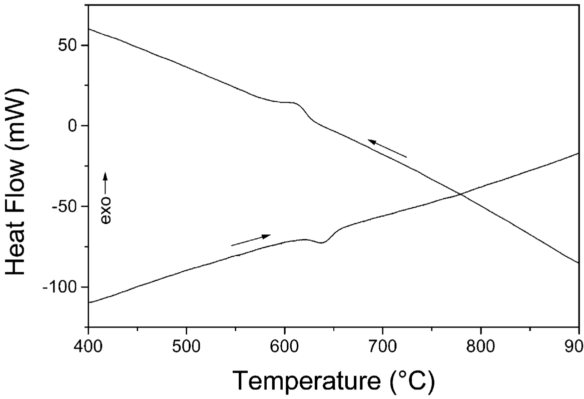

Fig. 8. DSC traces of SrA showing the endothermic monoclinic-hexagonal transformation on heating and the exothermic reverse transformation on cooling; heating and cooling rates: 5 °C/min.

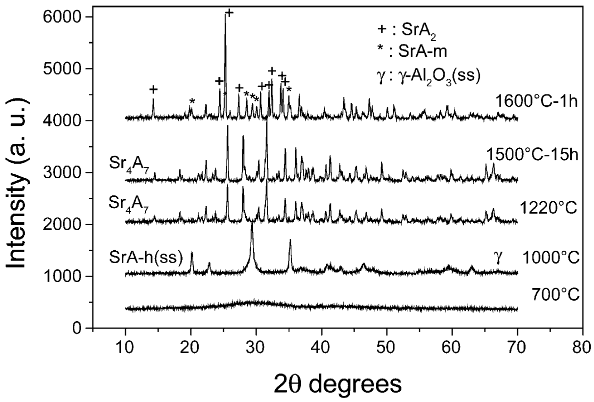

Fig. 9. XRD diagrams showing the formation of Sr_4A_7, via a mixture of hexagonal SrA solid solution and γ-Al_2O_3 solid solution, and its decomposition at high temperature into a mixture of SrA (monoclinic at room temperature) and SrA_2.

(Fig. 10) but heating beyond the second exothermic peak did not yield pure SrA_2. The sample was a mixture of SrA_2, as main phase, Sr_4A_7 and SrA_6. It is clear that by this thermal treatment the crystallisation of Sr_4A_7 is favoured at the detriment of SrA_2.

SrA_2 appears as a stable compound in the $SrO.Al_2O_3$ phase diagram.[3] However the stability of the dialuminate SrA_2 was questioned by Appendino[23] in 1972. Indeed this compound could be obtained only by solidification of the melt[4,23–25] while it was not formed by solid state reaction at 1400 or 1550 °C[23] nor at 1600 °C.[26] Moreover Appendino[23] observed that long annealing times at 1400 °C (200 h) resulted in its partial decomposition. He concluded that the dialuminate was metastable and could be obtained only from the melt or that its stability domain was restricted to a narrow temperature scale close to its melting point (~1800 °C). The synthesis by Lindop et al.[27] of monocrystals grown by Czochralski technique confirmed the stability of SrA_2 at very high temperatures, near the melting point.

By a careful study of the crystallisation of SrA_2 and Sr_4A_7[8,21,22] we arrived to the following conclusions:

- SrA_2 is a stable compound and may be obtained as pure phase by cooling the high temperature melt or by heating the amorphous precursor, but it is characterised by a slow kinetics of formation. It is metastable between ~1100 °C and a temperature close to its melting point (~1800 °C).
- Sr_4A_7 is stable between ~1100 and 1500 °C.[8,22] At higher temperatures it decomposes into a mixture of SrA and SrA_2 (Fig. 9). The latter, being not stable in this domain of temperature, decomposes slowly in its turn into a mixture of SrA and SrA_6 by long annealing or more rapidly by increasing the temperature, as reported by Appendino.[23]
- SrA_2,[8,21] with a low kinetics of formation, may be obtained pure by slow heating the amorphous precursor. At 0.5 °C/min it crystallises at ~900 °C without any intermediary metastable phase. It can also be obtained as single phase via the two metastable solid solutions, hexagonal SrA-h and γ-Al_2O_3, by annealing this mixture in the 950–1000 °C temperature range. That means that the temperature, associated with the low kinetics of formation, is essential in the synthesis of SrA_2. If no sufficient time is allowed for the complete formation of SrA_2, as the temperature raises beyond ~1100 °C, Sr_4A_7 will crystallise. At the heating rate of 5 °C/min, for the precursor of composition $4SrO.7Al_2O_3$, Sr_4A_7 is formed as single phase at ~1135 °C (Figs. 4 and 9), while for the sample of composition $SrO.2Al_2O_3$ a mixture of SrA_2, Sr_4A_7 and SrA_6 is obtained (Fig. 10). The behaviour at the solidification from the melted composition is similar. By controlled cooling (4 °C/min) to 1700 °C and then quenching to room temperature pure SrA_2 was obtained wile by direct quenching from the liquid state (~600 °C/s) a mixture of phases was obtained again.[8,21]

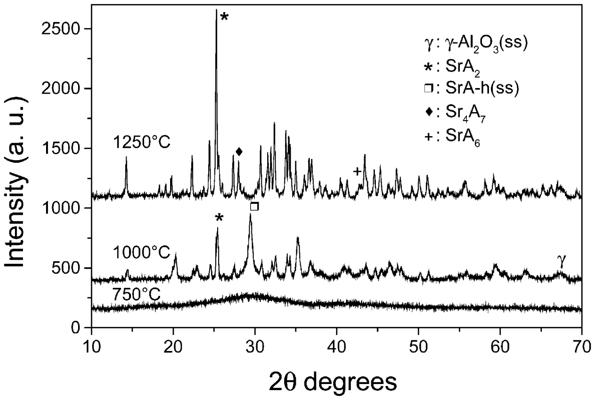

Fig. 10. XRD patterns obtained after heating at 5 °C/min an amorphous precursor of composition "$SrO.2Al_2O_3$" to the indicated temperatures.

- It is to be noted a supplementary and unusual behaviour for the amorphous precursors of SrA_2 and Sr_4A_7. Usually spray-dried amorphous precursors of alumina rich oxides are chemically very homogeneous and do not necessitate any other treatment before heating for crystallisation. However these two precursors are very sensitive to mechanical treatment. So after a simple manual grinding of the powder in an agate mortar, the precursor of SrA_2 crystallises directly at ~900 °C into single phase SrA_2, at a heating rate of 5 °C/min, while the precursor of Sr_4A_7 crystallises into a mixture of SrA_2 and SrA.[8,21] The free energy of the two systems must be very close and a little amount of energy brought by grinding can completely modify the scheme of crystallisation, into SrA_2 versus into the mixture of the two solid solutions SrA-h and γ-Al_2O_3. The understanding of this unusual behaviour needs a careful study of the local structure of the amorphous powders.

The crystallisation of the metastable hexagonal SrA solid solution stabilised by excess Al atoms is dominating for a wide scale of compositions of spray-dried powders. It results in the easy formation of Sr_4A_7. This was the case for two intermediary compositions studied as examples: $SrO.3Al_2O_3$, noted "*SrA*$_3$", and $2SrO.3Al_2O_3$, noted "*Sr*$_2$*A*$_3$" (Figs. 4, 5 and 11). After the second exothermic peak, for "*SrA*$_3$", besides SrA_6 and SrA_2, SrA and Sr_4A_7 are present (Fig. 11), while for "*Sr*$_2$*A*$_3$" a mixture of SrA, SrA_2 and Sr_4A_7 can be found. Mixtures corresponding to the phase diagram

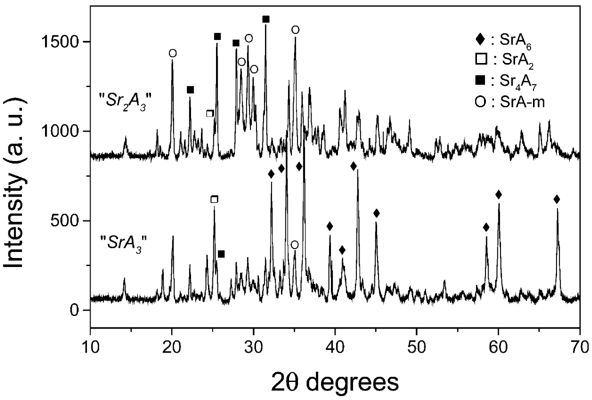

Fig. 11. XRD patterns obtained after the DSC analyses of two compositions surrounding SrA_2; S_4A_7 is present in the two mixtures.

established by Massazza,[3] i.e. SrA_6 and SrA_2 for "*SrA_3*", SrA and SrA_2 for "*$SrA_{1.5}$*" can be obtained by controlled cooling from the melt, by slow heating the precursor powders or still after grinding the amorphous powders.

3.3.4. *Strontium rich compositions*

Yamaguchi et al.[9] reported the synthesis of a new compound, $Sr_{12}A_7$, analogous to $C_{12}A_7$ in the $CaO.Al_2O_3$ system. For this they hydrolysed strontium and aluminium alkoxides. The differential thermal analysis, at 10 °C/min, revealed exothermic and endothermic peaks at 840–900 °C and 1035–1120 °C respectively. The exothermic peak was found to result from the crystallisation of $Sr_{12}A_7$, and the endothermic peak was found to result from the decomposition of $Sr_{12}A_7$ into Sr_3A and SrA. The DSC curve, at 5 °C/min, of the spray-dried amorphous powder of this composition (Fig. 5) is quite similar to their DTA curve with an exothermic peak between 820 and 840 °C and a wide and weak endothermic peak between 950 and 1050 °C. However, the XRD diagram of the sample just heated to 850 °C (Fig. 12) did not reveal the presence of $Sr_{12}A_7$ (JCPDS file 40-0025).[9] SrA and Sr_3A were already present with traces of an unidentified phase. After heating to 1200 °C the sample was a mixture of better crystallised SrA and Sr_3A. This mixture corresponding to the phase diagram is reached more rapidly by spray-drying nitrates solutions than by sol-gel with alkoxides as reported by Yamaguchi.[9]

Sr_3A is a stable compound, isostructural with C_3A ($Ca_3Al_2O_6$). It crystallises below 700 °C, when the nitrates are completely decomposed, and no amorphous precursor can be obtained for this composition and other strontium-richer compositions, like Sr_4A, which are not stable in moist atmosphere. For the composition $10SrO.3Al_2O_3$ corresponding to the new compound $Sr_{10}A_3$ described by Kalhenberg,[10] the XRD diagram of the spray-dried sample, heated to 1500 °C for 1 h, indicated the only presence of Sr_3A and β-Sr_4A, according to the phase diagram after Massazza.[3]

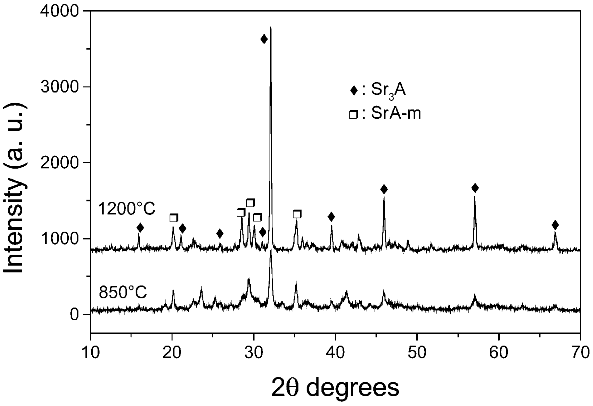

Fig. 12. XRD diagrams of the amorphous precursor of composition $12SrO.7Al_2O_3$ after heating to 850 and 1200 °C; no trace of "$Sr_{12}A_7$" was detected, the sample was a mixture of SA and S_3A, according to the phase diagram after Massazza.[3]

4. Conclusion

By decomposition of nitrates, amorphous precursors can be obtained for the compositions ranging from $12SrO.7Al_2O_3$ to Al_2O_3. The monoaluminate SrA is directly crystallised through a single exothermic peak. For all the alumina-richer compositions, at a heating rate of 5 °C/min, the formation of the stable compounds is performed via the crystallisation of metastable solid solutions of hexagonal SrA, stablised by excess aluminium cations, or γ-Al_2O_3 stabilised by strontium cations, or even the two solid solutions. The hexa-aluminate SrA_6 is obtained as single phase at relatively low temperature through γ-Al_2O_3 solid solution.

SrA_2 and Sr_4A_7 are competing with each other for crystallisation. At a usual heating rate of 5 °C/min Sr_4A_7 is easily formed at 1100–1150 °C but it is decomposed at temperatures higher than 1500 °C. On the other hand SrA_2, having a slow kinetics of formation, may be crystallised directly at 900–1000 °C by slow heating. It can also be crystallised directly at 5 °C/min heating rate if some energy, from grinding, is brought to the amorphous precursor.

Acknowledgements

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References

1. Smets, B., Rutten, J., Hoeks, G. and Verlijsdonk, J., $2SrO.3Al_2O_3:Eu^{2+}$ and $1.29(Ba,Ca)O.6Al_2O_3:Eu^{2+}$ two new blue-emitting phosphors. *J. Electrochem. Soc.*, 1989, **136**, 2119–2123.
2. Pallila, F. C., Levine, A. K. and Tomkus, M. R., Fluorescent properties of alkaline earth aluminates of the type MAl_2O_4 activated by divalent ions. *J. Electrochem. Soc.*, 1968, **115**, 642–644.
3. Massazza, F., The system SrO–Al_2O_3. *Chim. Ind. (Milan)*, 1959,

41, 108–115, and Levin, E.M., Robbins, C.R. and McMurdie, H.F., *Phase Diagrams for Ceramists*, ed. M.K. Reser, American Ceramic Society, Colombus, OH, 1964, Fig. 294.

4. Massazza, F. and Cannas, M., Research on the system CaO–Al_2O_3–SrO. *Ann. Chimica (Rome)*, 1959, **49**, 1342–1351.
5. Nadezhina, T. N., Pobedimskaya, E. A. and Belov, N. V., Coordination polyhedra of strontium in the structures sodium strontium germanate $Na_4SrGe_3O_3[GeO_4]_3$, strontium germanate $Sr_3[Ge_3O_9]$, strontium aluminate $Sr_4Al_4O_2[Al_{10}O_{23}]$ and bis(hydroxystrontium) tetrahydroxycuprate(II) $Sr_2(OH)_2[Cu(OH)_4]$. *Kristallografiya*, 1980, **25**, 938–943 (*Sov. Phys. Crystallogr.*, 1980, **25**, 537–540).
6. Minquan, D., Wang, M. and Guanglie, L., Research on fluorescence spectra and structure of single-phase 4SrO. $7Al_2O_3$:Eu^{2+} phosphor prepared by solid-state reaction method. *Mater. Sci. Engin. B*, 1998, **57**, 18–23.
7. Lin, Y., Tang, Z. and Zhang, Z., Preparation of long-afterglow $Sr_4Al_{14}O_{25}$-based luminescent material and its optical properties. *Mater. Lett.*, 2001, **51**, 14–18.
8. Capron, M., *Synthèse et Caractérisation d'Aluminates et d'Aluminosilicates de la Température Ambiante Jusqu'au Liquide à Hautes Températures*. Thesis, University of Orléans, France, 2001.
9. Yamaguchi, O., Narai, A. and Shimizu, K., New compound in the system SrO–Al_2O_3. *J. Am. Ceram. Soc.*, 1986, **69**, C36–C37.
10. Kahlenberg, V., Synthesis and crystal structure of $Sr_{10}Al_6O_{19}$: a derivative of the perovskite structure type in the system SrO–Al_2O_3. *Mat. Res. Bull.*, 2002, **37**, 715–726.
11. Capron, M., Florian, P., Fayon, F., Trumeau, D., Hennet, L., Gaihlanou, M., Thiaudière, D., Landron, C., Douy, A. and Massiot, D., Local structure and dynamics of high temperature SrO–Al_2O_3 liquids studied by ^{27}Al NMR and Sr K-edge XAS spectroscopy. *J. Non-Cryst. Solids*, 2001, **293–295**, 496–501.
12. Douy, A. and Gervais, M., Crystallization of amorphous precursors in the calcia-alumina system: a differential scanning calorimetry study. *J. Am. Ceram. Soc.*, 2000, **83**, 70–76.
13. Douy, A., Stabilisation of transition aluminas by alkaline earth ions. In *Key Engineering Materials, Vols. 132–136*, eds. D. Bortzmeier, M. Boussuge, Th. Chartier, G. Fantozzi, G. Lozes and A. Rousset. Trans Tech Publications, Zurich, Switzerland, 1997, pp. 101–104.
14. Douy, A., Aqueous synthesis of forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$). *J. Sol-Gel Sci. Technol.*, 2002, **24**, 221–228.
15. Jaymes, I. and Douy, A., Homogeneous mullite-forming powders from spray-drying aqueous solutions. *J. Am. Ceram. Soc.*, 1992, **75**, 3154–3156.
16. Jaymes, I., Douy, A., Gervais, M. and Coutures, J. P., Crystallizations in the SiO_2–Al_2O_3 system from amorphous powders. *J. Sol-Gel Sci. & Technol.*, 1997, **8**, 415–418.
17. Douy, A., Synthesis of cordierite powder by spray-drying. *J. Non-Cryst. Solids*, 1992, **147 and 148**, 554–558.
18. Messing, G. L., Zhang, S.-C. and Jayanthi, G., Ceramic powder synthesis by spray pyrolysis. *J. Am. Ceram. Soc.*, 1993, **76**, 2707–2726.
19. Cinibulk, M. K. and Hay, R. S., Textured magnetoplumbite fiber-matrix interphase derived from sol-gel fiber coatings. *J. Am. Ceram. Soc.*, 1996, **79**, 1233–1246.
20. Ito, S., Banno, S. and Inagaki, M., Phase transition in $SrAl_2O_4$. *Z. Physik. Chem.*, 1977, **105**, 173–178.
21. Capron, M. and Douy, A., Strontium dialuminate $SrAl_4O_7$: synthesis and stability. *J. Am. Ceram. Soc.*, 2002, **85**, 3036–3040.
22. Capron, M., Fayon, F., Massiot, M. and Douy, A., $Sr_4Al_{14}O_{25}$ (S_4A_7): formation, stability and ^{27}Al high resolution NMR characterisation. *Chem. Mater.*, 2003, **15**, 575–579.
23. Appendino, P., Equilibres à l'état solide dans le système oxyde de strontium—oxyde de barium—alumine. *Rev. Int. Hautes Tempér. Réfract*, 1979, **9**, 297–302.
24. Lagerqvist, L., Wallmark, S. and Vestgren, A., X-ray study of the systems CaO–Al_2O_3 and SrO–Al_2O_3. *Z. Anorg. Chem.*, 1937, **234**, 1–16.
25. Boyko, E. R. and Wisnyi, L. O. G., The optical properties and structures of CaO.$2Al_2O_3$ and SrO.$2Al_2O_3$. *Acta Cryst.*, 1958, **11**, 444–445.
26. Batti, P. and Sloccari, G., One zone in the ternary system SrO–Al_2O_3–Fe_2O_3. I. The 1200° isotherm of the zone formed by alumina, ferric acid, strontium monoaluminate and strontium ferrite corresponding to an Fe/Sr ratio of one. *Ann. Chim. (Rome)*, 1967, **1200**, 57 777-804.
27. Lindop, A. J. and Goodwin, D. W., The refined structure of SrO. *$2Al_2O_3$. Acta Cryst.*, 1972, **B28**, 2625–2626.