

Synthesis by a solid state reaction of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ compound

J.A. Rodríguez-García^{a,*}, E. Rocha-Rangel^a, J. Torres-Torres^b and J. M. Almanza-Robles^b

^aUniversidad Politécnica de Victoria, Avenida Nuevas Tecnologías, Parque Científico y Tecnológico de Tamaulipas TECNOTAM, Carretera Victoria-Soto la Marina Km 5.5, Cd. Victoria, Tamaulipas, México, 87137 México

^bCINVESTAV - Unidad Saltillo, Carretera Saltillo-Monterrey Km 13.5, Ramos Arizpe, Coahuila, México, 2590 México

The synthesis and formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ in the system $\text{SrCO}_3\text{-Al}_2\text{O}_3\text{-SrSO}_4$ has been studied in the range of temperatures from 800 °C to 1400 °C using X-ray diffraction, thermo gravimetric, differential thermal and scanning electron microscopy analysis. Pellets of a mixture of 3 : 3 : 1 molar ratio of reactive grade Al_2O_3 , SrCO_3 and SrSO_4 respectively were prepared, by solid state sintering, the reactive powders were thoroughly mixed under high energy ball-milling, uniaxially pressed into cylindrical samples and pressureless-sintered. Additionally the densities of some samples that were heat treated for 10 h at 1200, 1300 and 1400 °C were determined by the Archimedes method. The powder mixture was analyzed by TGA and DTA from room temperature to 1200 °C. XRD patterns indicated the formation of $\text{Sr}_3\text{Al}_2\text{O}_6$ and SrAl_2O_4 as intermediate phases that nearly at the end of the process reacted with SrSO_4 to form $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$. The formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ was complete at 1150 °C as XRD and DTA analysis indicated. An increase in the heat treatment time promotes the formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ at lower temperatures. The $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ powders were composed of spherical particles of small agglomerates. Results of density measurement indicated that only 80% of the theoretical density was reached for a treatment at 1400 °C of 10 h, which indicated the difficulty to obtain a dense material.

Key words: Synthesis, $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ compound, Solid State Reaction, $\text{SrCO}_3\text{-Al}_2\text{O}_3\text{-SrSO}_4$ system.

Introduction

Mexico is one of the main worldwide producers of celestite (SrSO_4). There are several strontium compounds obtained from celestite such as carbonates, sulphides and oxides [1]. Strontium carbonate is widely used as a component in several applications such as; pyrotechnics compounds [2], anti-corrosive paints, aluminum alloys [3], permanent magnets and TV screens [4]. Recently the increase in the fabrication of plasma screens has reduced the demand for SrCO_3 , therefore an interest in the diversification of the use of strontium compounds has been enlarged, and such is the case of strontium aluminates. These strontium aluminates have several applications such as luminescence pigments [5-6] and CO_2 sensors in the range from 800 to 1000 °C [7]. Some of these compounds have potential applications as refractory materials since they are corrosion resistant at high temperatures [8]. There are some other strontium compounds that have not been properly studied. Information about the synthesis of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ is scarce and there are some discrepancies in the studies until now developed. The formation of a mixture of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ and $\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ has been reported when mixtures of CaCO_3 , SrCO_3 , $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$ are sintered at 1350 °C for 24 h [9]. The

formation of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ compound using mixtures of SrCO_3 , Al_2O_3 and SrSO_4 sintered at 1200 °C for 20 h has also been reported [10]. Teoreanu *et al.* [11] have reported the formation of this compound at temperatures between 1350 and 1400 °C where a strontium aluminate (SrAl_2O_4) was formed at 1000 °C as a transitory phase. In all of these studies information about the synthesis steps, the effect of heat treatment time and morphology of the phases were not reported. In this study the synthesis of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ as a function of the heat treatment time was studied as well as the morphology of the phases formed.

Experimental

The requisite amounts of grade reactive Al_2O_3 , SrCO_3 and SrSO_4 to form $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ were prepared. The mixture was homogenized in plastic jars with acetone and alumina balls by spinning for 4 h. The mixture was dried at 60 °C for 24 h. After drying the mixture was ground in a mortar to disintegrate agglomerates. Disk pellets of 3 and 20 mm in diameter were made by uniaxial pressing at 100 MPa. The samples 20 mm in diameter were heat treated from 800 to 1400 °C for time periods of 6 and 10 h in a tubular furnace (Thermolyne 54700). In order to study the evolutions of densification of the compound, the density was determined by the Archimedes method in pellets of 20 mm in diameter heat treated at 1200, 1300 and 1400 °C for 10 h. The samples were analyzed in a X-ray diffractometer (Philips TW-3040) with a monochromatic copper $\text{K}\alpha$ radiation an operating voltage of 50kV and a current of

*Corresponding author:
Tel : +834-172-0383, ext: 2310
Fax: +834-172-0383, ext: 2310
E-mail: jrodriguez@upv.edu.mx

30 mA. A scanning speed of $0.10^\circ 2\theta\text{min}^{-1}$ and a step size of 0.02° were used to examine the samples in the range of $10\text{--}80^\circ 2\theta$. The crystalline phases were identified by means of the JCPDS-International Centre for Diffraction Data. The samples were cross sectioned and polished using SiC grinding media from 80 to 2400 grit size. Then the samples were polished using a $1\ \mu\text{m}$ diamond paste, finally the samples were carbon coated and analyzed by scanning electron microscopy (Philips XL30/ESEM). A powder sample of the mixture was analyzed by thermal gravimetric analysis (Perkin-Elmer ATG-7) from room temperature to 1200°C at 10°Cmin^{-1} . Pellet disks of 3 mm of diameter were analyzed by differential thermal analysis (Perkin-Elmer 1700) from room temperature to 1200°C at 10, 5 and 3°Cmin^{-1} (Curve B, C y D).

Results and Discussion

Fig. 1 shows a thermal gravimetric analysis (TGA) curve for the mixture of $\text{SrCO}_3\text{--Al}_2\text{O}_3\text{--SrSO}_4$. It can be observed that there is a 14.5% weight loss between 750 and 1050°C . This weight reduction corresponded to the decomposition of SrCO_3 to SrO and CO_2 .

Fig. 2 shows the results of differential thermal analysis (DTA) for the powder and disk samples of the $\text{SrCO}_3\text{--Al}_2\text{O}_3\text{--SrSO}_4$ mixture from room temperature to 1200°C . An exothermal peak was observed between 840 and 860°C for all the samples at different running conditions (A: powder sample at 10°Cmin^{-1} , B: pellet sample at 10°Cmin^{-1} , C: pellet sample at 5°Cmin^{-1} and D: pellet sample at 3°Cmin^{-1}), which corresponds to the thermal decomposition of SrCO_3 as is indicated in the TGA curve. In the same figure a change in slope is observed for all the running conditions at about 1100°C , this slope is more pronounced for the pellet samples and for the low heating treatments. For the curves C and D (pellet samples at 5 and 3°Cmin^{-1} , respectively) two extra peaks are observed, the first corresponds to an exothermic peak between 1105 and 1120°C . The second peak corresponds to an exothermal peak at 1150°C .

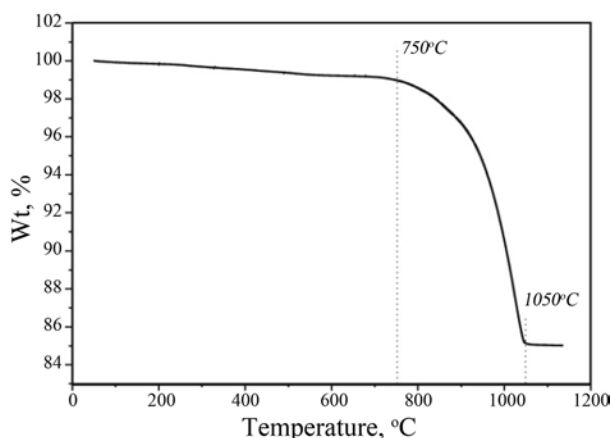


Fig. 1. TGA curve for a powder sample of a mixture of $\text{SrCO}_3\text{--Al}_2\text{O}_3\text{--SrSO}_4$ heat treated at 10°Cmin^{-1} .

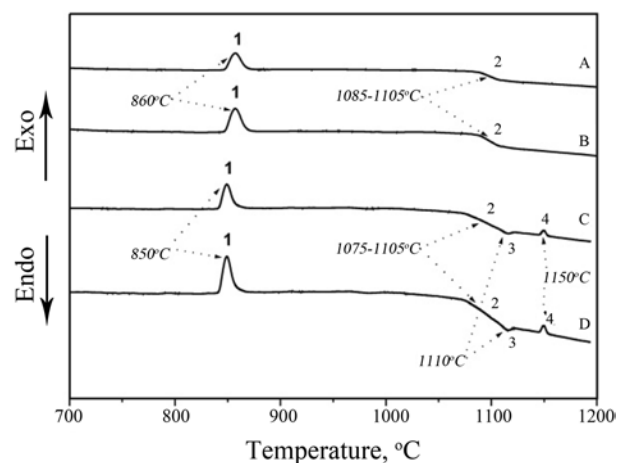


Fig. 2. DTA curves for samples or a mixture of $\text{SrCO}_3\text{--Al}_2\text{O}_3\text{--SrSO}_4$. (A) correspond to powder sample at 10°Cmin^{-1} ; (B), (C) and (D) correspond to pellet samples at 10, 5 and 3°Cmin^{-1} , respectively.

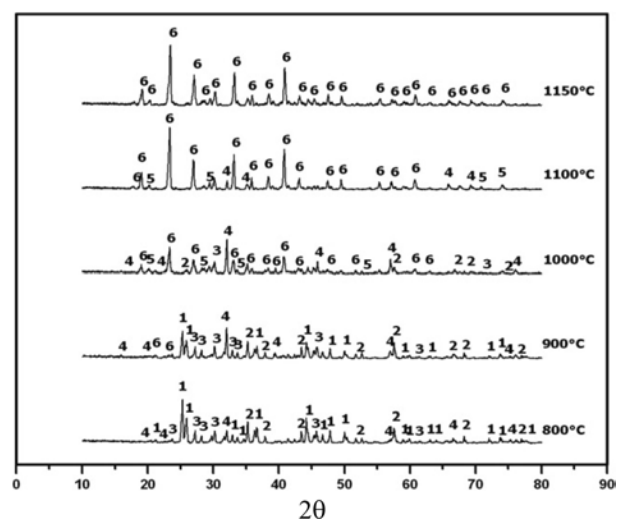


Fig. 3. X ray patterns for samples heat treated at several temperatures for 6 hours. 1: SrCO_3 , 2: Al_2O_3 , 3: SrSO_4 , 4: $\text{Sr}_3\text{Al}_2\text{O}_6$, 5: SrAl_2O_4 and 6: $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$.

Fig. 3 shows the X-ray diffraction (XRD) patterns for samples heat treated from 800 to 1150°C for 6 h. The sample sintered at 800°C mainly shows the presence of the initial raw materials and the formation of a strontium aluminate ($\text{Sr}_3\text{Al}_2\text{O}_6$) was detected. As the temperature was increased (900°C) the intensity of the peaks corresponding to the $\text{Sr}_3\text{Al}_2\text{O}_6$ increased and small peaks corresponding to the formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ were detected. At 1000°C and increase in intensity of the peaks corresponding to the $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$, was observed the formation of SrAl_2O_4 was detected as has been reported in the literature [9]. As the temperature was increased the peak intensities corresponding to strontium aluminates decreased (1100°C) and the peak intensities for the strontium sulfoaluminate increased, finally at 1150°C $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ was detected as a pure phase. These results showed that two strontium aluminates were formed as transition phases during the formation of the compound $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$,

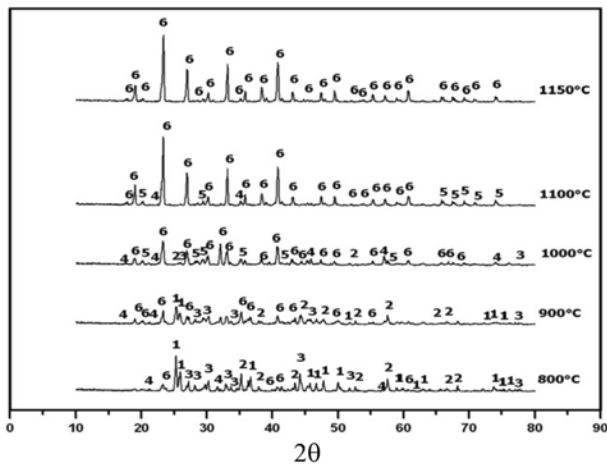
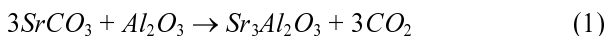


Fig. 4. X ray patterns for samples heat treated at several temperatures for 10 hours. 1 : SrCO_3 , 2 : Al_2O_3 , 3 : SrSO_4 , 4 : $\text{Sr}_3\text{Al}_2\text{O}_6$, 5 : SrAl_2O_4 and 6 : $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$.

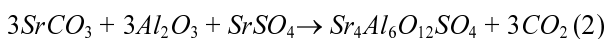
which is formed simultaneously.

Fig. 4 shows the XRD patterns for the samples heat treated from 800 to 1150 °C for 10 h. The XRD patterns showed only a slight difference compared to the samples heat treated for 6 h. With a longer period of time the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ compound starts to form at a lower temperature (800 °C), and as the temperature was increased the peak intensities corresponding to $\text{Sr}_3\text{Al}_2\text{O}_6$ decreased in comparison with samples heat-treated for 6 h. The $\text{Sr}_3\text{Al}_2\text{O}_6$ was not detected at 1100 °C while it was present for the treatment for 6 h. Longer periods of heat treatment allow the reaction to take place. The reaction is complete at 1150 °C for the treatments for 6 and 10 h. The results of XRD show that two strontium aluminates were formed between 900 and 1000 °C, however DTA analysis did not demonstrate any peaks that correspond to the formation of these compounds. Therefore the first slope can be related to the reaction of $\text{Sr}_3\text{Al}_2\text{O}_6$ to form $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ and the peak observed around 1120°C can be related to the reaction of the SrAl_2O_4 to form $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$. The peaks located at 1150 °C correspond to the formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$. In this way the reaction steps from the strontium sulfoaluminate can be written as follows:

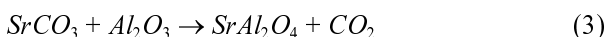
At 800 °C, as SrCO_3 started to decompose it reacts with alumina to form a strontium aluminate:



At 900 °C the formation of strontium sulfoaluminate started:



Between 1000 and 1100 °C the second aluminate started to form:



Finally, between 1100 and 1150 °C the strontium aluminates reacted to form strontium sulfoaluminate:

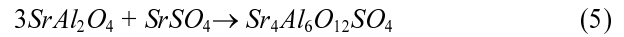
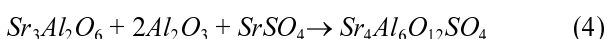


Fig. 5 shows the scanning electron microscopy (SEM) analysis for a typical sample of the mixture of SrCO_3 - Al_2O_3 - SrSO_4 , heat treated at 1000 °C for 6 h. Fig. 5a shows an EDS analysis carried out on the spherical particles, according to the semi quantitative analysis they correspond to $\text{Sr}_3\text{Al}_2\text{O}_6$ (Sr : 63.7%, Al : 13.07%, O : 23.25%). Fig. 5b shows the EDS analysis realized in different phases that coexist in the microstructure of the sample. Spherical particles correspond to $\text{Sr}_3\text{Al}_2\text{O}_6$ as has been commented, a second phase found in the microstructure corresponds to SrAl_2O_4 (Sr = 42.60%, Al = 26.24%, O = 31.13%) in agreement with the EDS analysis. The presence of this compound was corroborated by XRD analysis as shown in the Figs. 3 and 4.

Fig. 6 shows micrographs of the SrCO_3 - Al_2O_3 - SrSO_4 mixture heat treated at 1100 °C for 6 and 10 h. In Fig. 6a semispherical particles can be observed formed by agglomerates that correspond to $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ (Sr : 43.8%, Al : 20.21%, O : 31.9%, S : 3.9%) according to the EDS analysis. As the heat treatment time is increased it was observed

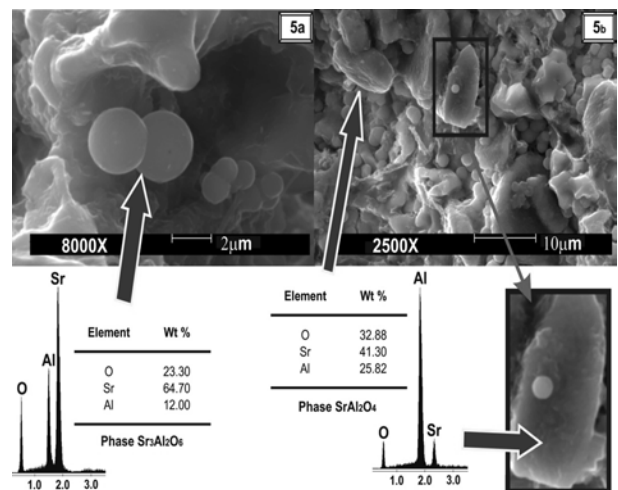


Fig. 5. Compounds found in a sample sintered at 1000 °C for 6 hours. 4 : $\text{Sr}_3\text{Al}_2\text{O}_6$, 5 : SrAl_2O_4 and 6 : $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$.

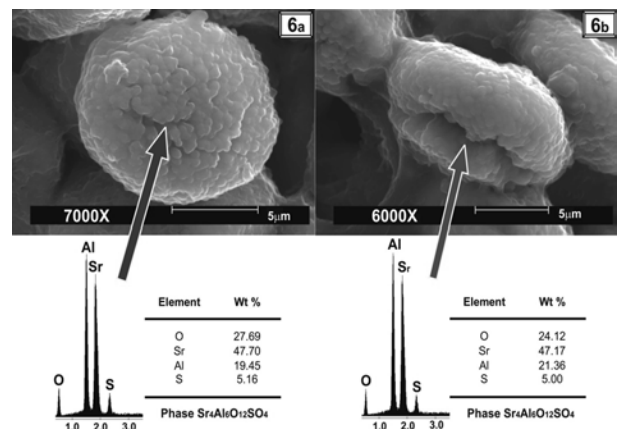


Fig. 6. Compounds found in samples sintered at 1100 °C for 6 and 10 hours. 6 : $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$.

a neck growing typical of an intermediate stage of sintering was observed (Fig. 6b). It appeared that a glassy phase was formed between particles.

The maximum density obtained for a sample that was sintered at 1400 °C for 10 h was 2.886 grcm^{-3} , which is about 80% of the theoretical density. The values of density for samples sintered for 10 h at 1200 and 1300 °C were 2.779 and 2.82 grcm^{-3} , respectively, these density values indicate that the densification of this material is difficult to achieve, probably because during sintering there is competition between the reaction of formation of the desired product and densification of the same.

Conclusions

The $Sr_4Al_6O_{12}SO_4$ was synthesized by a solid state reaction after a heat treatment of 1150 °C for 6 and 10 h. Two transition phases $Sr_3Al_2O_6$ and $SrAl_2O_4$ were formed during the heat treatments and reacted with $SrSO_4$ at the end of the process to form $Sr_4Al_6O_{12}SO_4$. The morphology of the $Sr_3Al_2O_6$ corresponds to spherical particles (1-2 μm); the $SrAl_2O_4$ showed an indefinite form (5-10 μm) and the $Sr_4Al_6O_{12}SO_4$ corresponds to spherical particles formed of agglomerates of small particles (5-10 μm). The maximum

density obtained corresponded to 80% of theoretical for a sample sintered at 1400 °C for 10 h.

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