

Physical properties of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound

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The $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound was synthesized by a solid state reaction starting from stoichiometric mixtures of 3 : 3 : 1 molar ratio of reactive grade of SrCO_3 , Al_2O_3 and SrSO_4 , respectively. Cylindrical samples were confirmed by uniaxial pressing at 100 MPa and were heat treated at 1400 °C during 4 hrs. Subsequently, the samples were ground and re-conformed in cylindrical shape samples by uniaxial pressing at 300 MPa. The new samples were heat treated at 1400 °C during 24 hrs. This process was done in order to increase density of the samples. The $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound was characterized by the study of its physical properties such as: density, micro-hardness, thermal expansion and stability, enthalpy of formation, magnetic properties and electrical conductivity. Experimental results show that the maximum density obtained for the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound was 2.913 gcm^{-3} , with thermal expansion coefficient of $10.12\text{E}^{-06} (^\circ\text{C}^{-1})$; it also presents an enthalpy of 2.3 KJmol^{-1} and an excellent thermal stability at elevated temperatures in different atmospheres. In addition, the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound is neither electrically conductive nor magnetic.

Key words: Physical properties, Strontium compound, Solid state reactions, Ceramic materials.

Introduction

Strontium is one of the least known and investigated metals from the periodic table. It is found in nature as celestite (SrSO_4) and Mexico one of the largest producers worldwide. This mineral can be processed to form compounds such as; carbonates, nitrates and oxides [1] the most important being strontium carbonate (SrCO_3) which is used in applications ranging from production of picture tubes for color televisions [2-3], as a component in ceramic permanent magnets [4], pyrotechnics [5], antifouling paints and in the melting of aluminum alloys [6]. However, the demand of this material for its most important application (picture tubes) has significantly decreased with the advent of flat panel displays (Plasma, LCD, Diodes and LED's). On the other hand, celestite is being marketed as a mineral, without being processed and investigated for possible applications, either as sulfate, carbonate or other compound result of the reaction between related elements, not getting higher sales gains. Therefore, the study of new applications of the compounds of strontium is required. Previous studies have been made on strontium aluminates, a compound belonging to the

$\text{SrO-Al}_2\text{O}_3$ system, with diverse applications such as: luminescence pigments [7-8], CO_2 sensors [9-10] and refractory materials [11]. However, there are other strontium compounds whose physical applications are unknown because their study has been scarce and limited to certain synthesis of formations. One example of this is the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound reported in the literature as a synthesis of formations, employing a morphological study of the solid phases present in the process [12-14]. Thus, this paper aims to follow up the study of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound generating fundamental knowledge of its physical properties.

Materials and Methods

The reagents Al_2O_3 , SrCO_3 and SrSO_4 were mixed according to a proportion of 3 : 3 : 1 molar, respectively. The mixture was homogenized in plastic jars with acetone and alumina balls by spinning during 2 hrs. The resulting paste was dried in a muffle at 60 °C during 24 hrs and ground in a mortar for removing agglomerates. Cylindrical samples were made by uniaxial pressing using 100 MPa. The samples were dimensioned with 5 mm diameter by 2 mm thick to determine the enthalpy of formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound in a differential thermal analyzer (Perkin-Elmer DTA-1700). The experimental parameters were the application of temperature from 25 °C to 1200 °C at a heating rate of 3°Cmin^{-1} . Curves representing the changes in heat

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flow with increasing temperature, relating the area under the curve of the peak corresponding to the formation of the compound under study, mass and a calibration constant of the experimental equipment to determine the enthalpy of formation were recorded. Cylindrical samples were made by uniaxial pressing of 100 MPa. The samples were 20 mm in diameter by 3 mm thick and were heat treated at 1400 °C during 4 hrs in a tubular furnace (Thermolyne 54700), this in order to synthesize the compound under study. Subsequently, the samples were ground and re-conformed in cylindrical shape samples by uniaxial pressing at 300 MPa (same dimensions) and heat treated at 1200, 1300 and 1400 °C during 6, 12 and 24 hrs. Densities of the samples were determined using the volumetric displacement method proposed by Archimedes, comparing the results with those obtained in the mercury immersion method. The micro-hardness of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound was determined (cylindrical samples with maximum densification) using a micro-hardness tester (Wolpert Wilson Instrument 402MVD). The procedure consisted of applying a controlled load to samples using a diamond tip causing cracks in the corners of the indentation, corresponding lengths measured and related to the hardness of the material. The thermal stability of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound (cylindrical samples with maximum densification) was determined in different atmospheres using a thermo-gravimetric analyzer (Perkin-Elmer DTA-1700). The experimental parameters were the application of temperature from 25 °C to 1400 °C at 10 °Cmin⁻¹, with injection of gas (oxygen, nitrogen, compressed air and carbon dioxide) and the corresponding recording of curves of weight loss of samples. The thermal expansion of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound (cylindrical samples with maximum densification) was determined using a dilatometer (NETZSCH 402PC). The experimental parameters were the application of temperature from 25 °C to 1300 °C with a heating rate of 10 °Cmin⁻¹ and the result showed geometric changes samples in relation to the increase in temperature. The electrical conductivity of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound (cylindrical samples with maximum densification) was determined by using the impedance spectroscopy technique (Solartron 1260). The experimental parameters were the application of temperature at 550 °C with a heating rate of 10 °Cmin⁻¹ and variation in the frequency; the electrical response of the material was recorded afterwards. The magnetic property of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound (25 mg of powder) was determined in a vibrating sample magnetometer (Lakeshore 7307). Magnetic fields were applied to the samples at room temperature and hysteresis curves recorded in response to these fields.

Results and Discussion

The formation enthalpy of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound was determined in this exothermic peak in the curve obtained of DTA (Fig. 1). This property is determined by the area under the curve of such exothermic peak and the following equation:

$$\Delta H = KA/m \quad (1)$$

Where: K is a calibration constant established by the DTA equipment, A is the area under the analyzed peak curve and m is the mass of the sample. The differential enthalpy related to the formation of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ was 2.3 KJmol⁻¹, a relatively low value due to the gradual process of formation of this compound.

Table 1 shows the results obtained in the densification

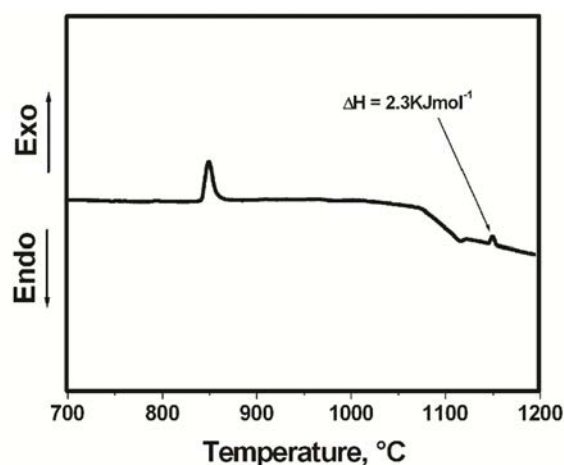


Fig. 1. Determining the formation enthalpy of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound registered in the exothermic peak at 1150 °C from DTA curve.

Table 1. Densities obtained from $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound in cylindrical samples, thermally treated at different conditions.

Temperature	Density, gcm ⁻³			
	Isotherm	6 hrs	12 hrs	24 hrs
1200 °C		1.758	2.784	2.796
1300 °C		2.246	2.843	2.881
1400 °C		2.617	2.896	2.913

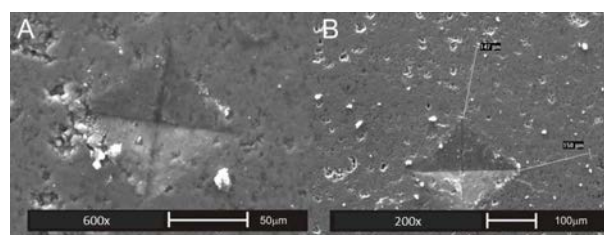


Fig. 2. Microphotographs of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound after the micro-hardness test. Remaining porosity is observed in the same, (A) and the crack propagation due to such porosity (B).

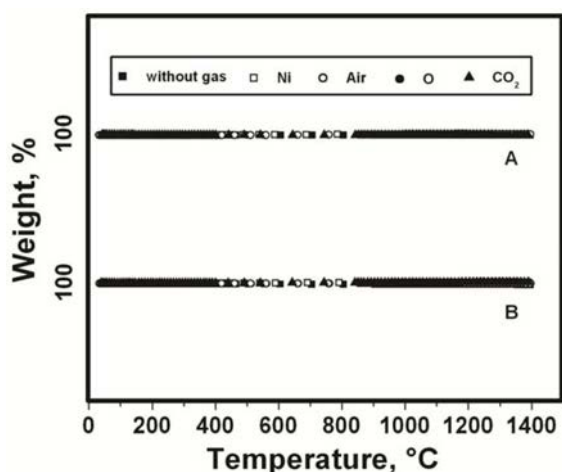


Fig. 3. Thermal stability curves of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound indifferent atmospheres. (A) samples sintered at 1400°C during 6h and (B) samples sintered at 1400°C during 24 hrs.

of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound in cylindrical samples thermally treated at different conditions. The densification increases as heat-treatment conditions increase. The maximum density was present in the heat-treated sample at the temperature of 1400°C with an isotherm of 24 hrs, which is about 81% of the theoretical density (3.6 grcm^{-3}).

Fig. 2 corresponds to two microphotographs of a sample analyzed in the micro Vickers hardness tester in order to determine the micro-hardness of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound. Recalling that the hardness of the ceramics is related to the length of the cracks which are formed at the time of indenter

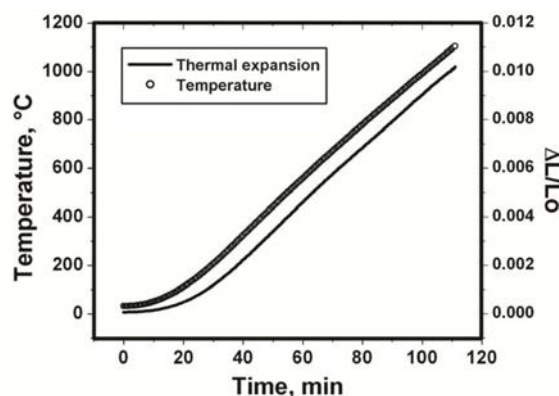


Fig. 4. Thermal expansion curve recorded for the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound. The linear behavior of the expansion of the ceramic compound is observed with respect to temperature increase.

penetration into the sample. However, its expansion is favored by the high percentage of porosity; therefore, these tests were omitted.

Fig. 3 shows the curves obtained from TGA corresponding to thermal stability studies of $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound (pellets heat-treated at 1400°C during 6 and 24 hrs. In general, the strontium compound exhibits good thermal stability in different atmospheres. However, note that the curves of group B have a light decomposition (weight loss about 0.2%) under nitrogen and minimal oxidation (weight gain about 0.1%) in atmospheres of oxygen and compressed air at 1400°C .

Fig. 4 shows the curve of thermal expansion that the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound presented by applying relatively high temperatures. This curve is

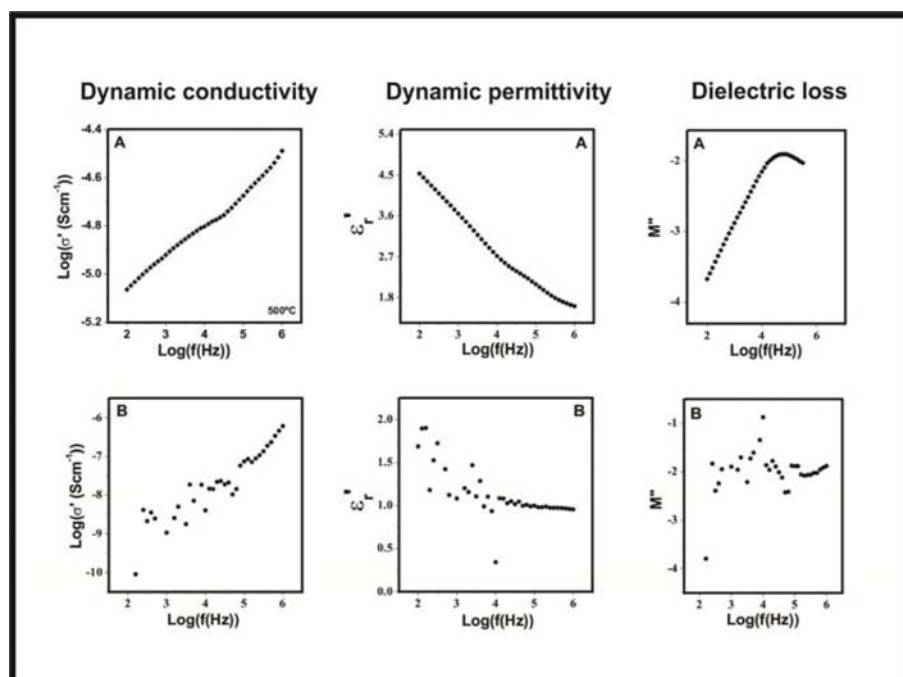


Fig. 5. Electrical behavior of two samples in the frequency response and temperature applied. (A) $\text{La}_{96}(\text{SiO}_4)_6\text{O}_{2.4}$ and (B) $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$.

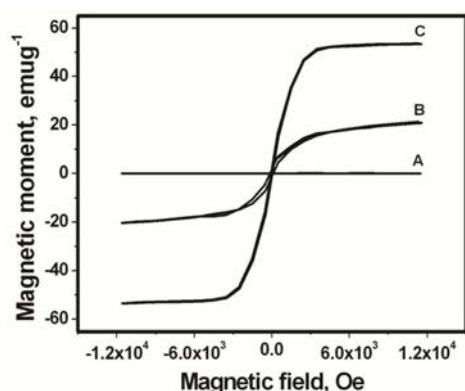


Fig. 6. Hysteresis curves of three samples in response to an applied magnetic field. (A) $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$, (B) FeO and (C) Ni .

related to the coefficient of thermal expansion which presents a value of $10.12 \times 10^{-6} (\text{°C}^{-1})$ that is on the average of the ceramic [15].

Fig. 5 presents results from the evaluation of the electrical conductivity of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound. Additionally, the curves of highly electrically conductive material were submitted for comparative purposes. Analyzing the curves of the compound under study (curve B) shows a large distortion between the values, a phenomenon that takes a linear trend with increasing frequency. Comparing these results with those obtained for compound $\text{La}_{96}(\text{SiO}_4)_6\text{O}_{2.4}$, which is a highly conductive ceramic, it is concluded that the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound does not present good electrical conductivity, considering that experimentation employs a relatively high temperature (550 °C).

Fig. 6 shows the results obtained regarding the magnetic properties of the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound. Additionally, this figure shows the results of two high magnetic compounds for comparative purposes. It is observed that the compound under study (curve A) showed no response to the applied magnetic field, compared to the curves of ferrous oxide and nickel, being the nickel a material with higher magnetization.

Conclusions

The $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound exhibited a value of enthalpy, corresponding to the last stage of formation, 2.3 kJmol^{-1} ; this being relatively low and because the formation of the compound under study is carried out gradually, from 850 °C to 1150 °C , very little energy is necessary in the final stage of formation. The highest density was 2.913 gcm^{-3} (81% compared to the theoretical value) which indicates that there is residual porosity in the cylindrical samples. It was concluded that for improving the densification of the

same compound it would be necessary to employ higher pressures, larger forming isotherms, and temperatures above 1400 °C , provided that the compound under study is stable (without decomposition and phase transformations). The thermal expansion was of $10.12 \times 10^{-6} (\text{°C}^{-1})$, value which is half the average of the ceramic materials. Excellent thermal stability was presented under different atmospheres and high temperatures. Furthermore, the $\text{Sr}_4\text{Al}_6\text{O}_{12}\text{SO}_4$ ceramic compound, under the experimental parameters used, did not show magnetic properties, does not conduct electricity in ionic form and does not present good mechanical properties (hardness).

Acknowledgments

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