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Sodyum Silikoflorürün Mikroyapı ve Isıl Davranışlarının İncelenmesi

Microstructural Study and Thermal Behavior of Sodium Silicofluoride

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Öz

Sodyum silikoflorür, Na_2SiF_6'nın kimyasal formülü ile son zamanlarda seramik, metalurji ve kimya mühendisliği gibi çeşitli endüstrilerde birçok uygulama alanı bulan inorganik sentetik bir malzemedir. Bu tozun en önemli kullanımlarından bazıları opal cam-seramik, sırlar ve fritlerdir. Uygulama alanlarının gün geçtikçe artmasına karşı, literatürde sodium silikoflorür (SSF) ile ilgili sınırlı sayıda kaynak mevcuttur. Bu araştırmada, ticari bir sodyum silikoflorür tozunun ısıl davranış ve mikroyapı açısından karakterize edilmiştir. Termal analiz, hava atmosferinde 900 °C'de diferansiyel termal ve termo gravimetri eğrilerine göre araştırılmıştır. Mikroyapısal analizler, taneciklerin tane büyüklüğü ve morfolojisini incelemek için taramalı ve geçirimli elektron mikroskopları kullanılarak yapılmıştır. Sonuçlar, ticari sodyum silikoflorür malzemesinin, eşlik eden bir endotermik reaksiyonla havada 430-600 °C sıcaklık aralığında çözündüğünü göstermiştir. Mikroyapısal karakterizasyonlarla, incelenen SSF tozunun granüler morfolojisi, altıgen şekilli prizmaların ve ilgili gözeneklerin varlığına da açıklık getirmiştir.

Anahtar Kelimeler
"Sodyum silicoflorür, Karakterizasyon, Termal analiz, Elektron mikroskobu."

Abstract

Sodium silicofluoride, with the chemical formula of Na_2SiF_6, is an inorganic synthetic material which recently found lots of applications in various industries such as ceramic, metallurgy and chemical engineering. One of the main important usages of this powder is in the production of opal glass-ceramics, glazes and frits. Despite the expansion of its applications, the properties of this material were not investigated deeply elsewhere. In this research, a commercial sodium silicofluoride powder was studied and characterized in terms of thermal behavior and microstructure. The thermal analysis was investigated according to the differential thermal and thermo gravimetry curves by heating the material up to 900 °C in air. The microstructural analyses were also performed using scanning and transmission electron microscopies to study the grain size and morphology of the particles. The results showed that this commercial sodium silicofluoride material is decomposed in the temperature range of 430-600 °C in air by an accompanied endothermic reaction. The microstructural characterizations were also clarified the granular morphology of the studied SSF powder, existence of the hexagonal shaped prisms and associated pores.

Key Words
"Sodium silicoflouride, Characterization, Thermal analysis, Electron microscopy."

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1. Introduction

Fluorosilicate materials are the group of chemical compounds that are termed as complex fluorides. The typical chemical formula is as M_2SiF_6 and $NSiF_6$ where M and N could be any of the alkali or alkaline earth ions, respectively (Coyle et al., 1981). Sodium fluorosilicate (SSF) is also known as sodium hexa fluorosilicate, sodium fluosilicate and sodium hexa fluosilicate, is an inorganic synthetic mineral (Kumar et al., 2010). The crystal structure of sodium silico-fluoride consists of two octahedral of $[SiF6]^{2-}$ accompanied by two independent sodium cations (Zhang et al., 2017). It is a colorless, odorless and tasteless powder having hexagonal crystal structure. It is soluble in ether and insoluble or weak soluble in most of the alcohols such as ethanol and isopropanol. The solubility of this matter is greater in acid rather than in water. Precipitation process is a general route for the production of sodium fluosilicate fine crystals, using sodium chloride or sulphate solutions and fluosilicic acid as raw materials. Crystallization of sodium fluosilicate happens immediately when starting chemicals are mixed (Toure et al., 2012). It decomposes in alkaline solution and produces sodium fluoride (NaF) and silicon dioxide (SiO_2) (Ciavatta et al., 1988). All the alkali, alkaline earth type silicofluoride chemicals would lose SiF_4 during thermal decomposition according to the following reactions:

$$M_2SiF_6 \longrightarrow 2MF + SiF_4 \quad (1)$$
$$NSiF_6 \longrightarrow NF + SiF_4 \quad (2)$$

Generally, the decomposition temperatures of these types of compounds range from 300 and 700 °C which may depend to the atmosphere. SSF is also decomposed to sodium fluoride and silicon tetrafluoride (SiF_4) by heating at 300 °C. It is generally noxious and its dust may cause irritation of eyes, skin, and mucous membranes (Smith, 1985). Nowadays, SSF has found lots of applications in various products and industries. It is used in the production of the opal glasses and vitreous enamels as opacifier, aluminum casting as foundry additives, welding electrodes and powders as cover flux and wood preservation as coagulator (Khan et al., 2015).

It has also wide applications in the insecticides and pesticide industry, fluoridation of potable water, fluorinating agent in pharmaceutical industry such as toothpaste, coagulant agent for latex, hygroscopic agent of acid resistant concrete, acidifying agent in textile finishing and leather industry for pre-treatment of hides before tanning (Hattab, 1987; Smith, 1985). Recently it was reported the usage of SSF powder in some advanced applications such as cryolite production, coated papers, foam production, filler for bonded abrasives, rubber tires and acid clay manufacturing. As an important fluorosilicate chemical, sodium fluorosilicate has also received considerable attention high-tech products and synthesis over the past decades (Yeo et al., 2016). It was widely used as a versatile template to synthesize $NbSi_2$ films, Si_3N_4 fibers, Si nanowires, red phosphors and Pt nanotubes (Arai et al., 2011; Jeong et al., 2010). Table 1 lists some of the general specifications of the sodium silicofluoride material. Figure 1 also shows the schematic hexagonal structure of this inorganic compound.

Table 1. Specifications of sodium silicofluoride.

Chemistry	Na_2SiF_6
Molar mass	188.05 g/mol.
Crystallography	Hexagonal
Density	2.7 g/cm³

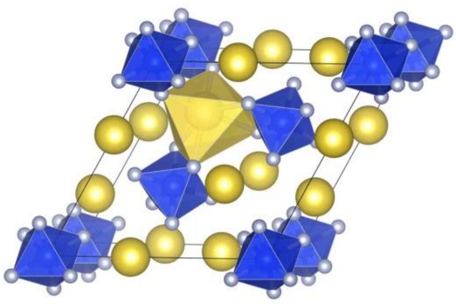

Figure 1. Crystal structure of sodium silicofluoride.

Although SSF material has found recently many industrial applications, but its properties were not investigated deeply in literature. On the other hand the application of this material is gradually increasing in ceramic industry such as the production of opal glasses, enamels, frits and other advanced ceramic materials such as nitrides (Andreeva et al., 1986). In this regard, the understanding of thermal behavior and microstructural properties of this material would be a key-point for ceramic scientist to develop the new technological performance and application for this material. There are some reports in literature on thermal characterization of SSF powder (Vanka et al., 1980). However, according to the knowledge of authors, there are rare studies on the characterization of commercial products. In this research, a commercial sodium silicofluoride powder was supplied and investigated in terms of thermal analysis (DTA/TGA/DTG) in air do reveal the decomposition behavior by heating. Also the morphology and grain size of the product were investigated using scanning and transmission electron microscopy (SEM/TEM) techniques.

2. Experimental Procedure

Sodium silicofluoride (SSF) sample was delivered from Arya Tabalvor Arvand Co. (Abadan, Iran) as a granular white powder. The technical properties of the sample are summarized in Table 2 according to the data sheet. The as-received powder was used in the characterization tests without further purification or chemical processing. The powder was previously dried in an electric oven at 105 °C for 12 h, milled and passed through a 200 µm sieve to obtain a homogeneous sample.

Table 2. Characteristics of the studied sodium silicofluoride sample.

Purity (wt. %)	> 99.2
Density (g/cm^3)	2.679
Fe (wt. %)	0.01
Pb (ppm)	10
Loss/105 °C (wt. %)	0.30
< 40 mesh (wt. %)	99
> 325 mesh (wt. %)	5

Thermal decomposition was studied via differential thermal analysis (DTA), thermo-gravimetry (TG) and differential thermo-gravimetry (DTG) on a TA 7000 thermal analyzer (Hitachi, Japan). Around 35 mg of powder was poured in a platinum cell and heated with the rate of 5 °C min^{-1} up to 900 °C in air. Microstructure and morphology of the sample was investigated using a FEG 250 field emission scanning electron microscope (FE-SEM, QUANTA, Czech). For sample preparation, a small amount of powder was dispersed into distilled water, spread on a carbon bond and then coated with a thin layer of gold-platinum using a sputtering coater. A JEM 2100 transmission electron microscope (TEM, JEOL, Japan) working at 200 kV equipped with an energy dispersive spectroscope (EDAX, Oxford, UK) was employed for accurate microstructural analysis. TEM sample was prepared by ultrasound dispersion of SSF powder into isopropanol alcohol, putting a small drop onto a 200 mesh copper grid and covering it by an amorphous carbon film. The micrographs have been taken in the bright field (BF) mode.

3. Results and Discussion

Figure 2 shows the thermal behavior of sodium silicofluoride sample which was heated up to 900 °C in air. The differential thermal analysis (DTA), thermo-gravimetry and differential thermo-gravimetry curves are shown in this picture. Table 3 lists the summary of the thermal analysis data according to the DTA, TG and DTG curves. As it is clearly seen in the thermal analysis curves of Figure 2, there is an important phenomenon in the temperature range of 500-600 °C. DTA curve shows an endothermic peak at 563 °C, while the maximum temperature was detected equal to 577 °C from DTG. According to the TG curve, the thermal decomposition of studied sodium silicofluoride material started at 432 °C and after 55.46 wt.% weight loss, completed at 596 °C. The thermal decomposition of fluosilicates of alkaline and earth alkaline metals happen in the range of 300-700 °C. It was mentioned before that 1 mole of sodium fluosilicate (Na_2SiF_6) would be decomposed to 2 moles of sodium fluoride and 1 mole of silicon tetrafluoride as decomposition products by heating (Yeo et al., 2016). Sodium fluoride (NaF) is a stable salt which remains after reaction as a solid product. However, silicon tetra fluoride (SiF_4) is a gas product and would evaporate after decomposition. Theoretically, the accompanied weight loss of the reaction should be around 55.32 wt.% which is closed to the obtained value from TG. The decomposition temperature of sodium silicofluoride could have important effects on the desired applications and properties of the produced products. This temperature, as it is clear in the obtained thermal analysis results, could vary in different ranges of heat (300-650 °C) (Vanka et al., 1980).

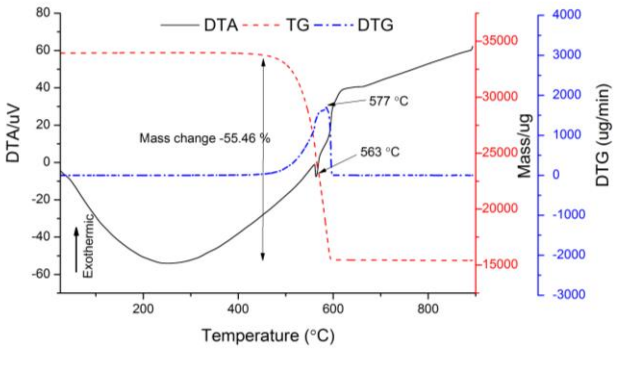

Figure 2. Thermal analysis curves of sodium silicofluoride after heating in air up to 900 °C.

The thermal analysis results show that the decomposition phenomena of SSF could not happen in a sharp temperature which is attributed to the impurity presence in the commercial product and also kinetically criteria of the reaction. Generally the decomposition reaction could start from the surface of SSF grain and push forward from surface to the core of the particles. The formation of NaF layer (solid product of the decomposition reaction) on the surface of the sodium silicofluoride particles could decrease the diffusion rate and act as a barrier for SiF_4 gas to remove out. This phenomenon could control the speed of composition and lasting the needed time of the reaction to be completed. On the other hand, it could be said that the complement of the reaction and transformation of all sodium silicofluoride material could be postponed to the higher temperatures (500-650 °C) rather than the thermodynamical expectations. The temperature range of thermal decomposition of sodium silicofluoride could be a kind of an important issue in the thermal regime designing and production of some kinds of ceramics such as opal glasses and glass-ceramics using SSF as raw materials.

Table 3. Thermal analysis data.

Average reaction temperature, DTA	563 °C
Reaction temperature range, TG	432-596 °C
Average reaction temperature, DTG	577 °C
Weight loss, TG	55.46 wt.%

Figure 3 shows the scanning electron microscopy micrographs and morphology of the studied sodium silicofluoride powder at different magnifications. Figure 3 (a) shows the morphology and size of the SSF particles at lower magnification. As it is visible in this figure, this commercial SSF powder was produced in the granular form which shows a wide distribution of particle sizes in the range of 10-50 um. The size of the granules is strongly depended on the production process of the powder, thermal regime of the calcination and drying process of the commercial SSF products. Figure 3 (b) also shows the morphology of a granule under higher resolution. As it is clear, the granule consisted of the grown hexagonal prisms with some visible pores on the section profiles of the rods. Figure 4 (a) shows the high-resolution transmission electron images of the studied commercial sodium silicofluoride powder. The hexagonal shapes of prism are also clear in this image. Figure 4 (b) demonstrates the line scan chemical analysis of the grain from center toward out of the particle. According to the theoretical chemical formula, the main constitutional elements of the silicofluoride of the sodium are sodium (Na), silicon (Si) and fluorine (F) with the weight percentage of 24.47, 14.89 and 60.64 (Arai et al., 2011). The major elements were also detected as Na, Si, and F. Oxygen and calcium elements were also characterize and detected in the EDAX chemical analysis of the commercial SSF sample and could be attributed to the presence of the some oxide impurities such as calcium oxide (Coyle et al., 1981).

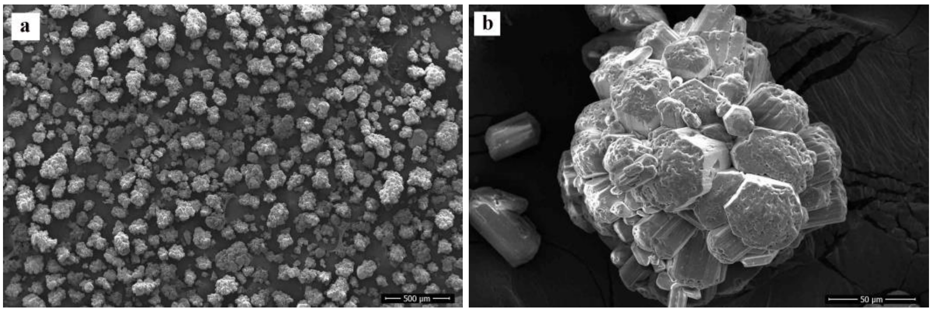

Figure 3. Scanning electron microscope images and morphology of sodium silicofluoride powder.

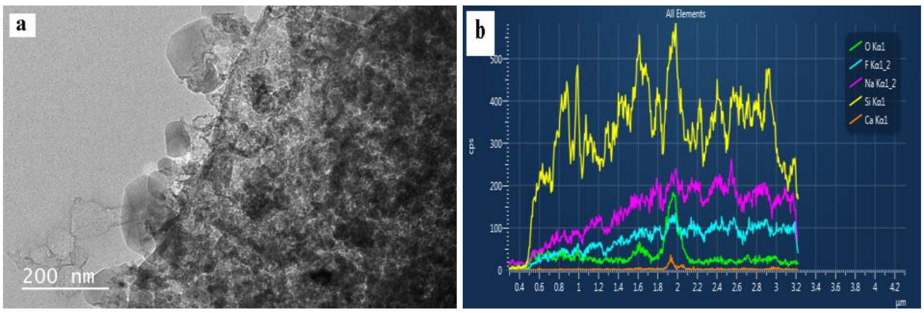

Figure 4. Transmission electron microscopy micrograph and EDAX chemical analysis of sodium silicofluoride.

The granular shape of the commercial SSF particle could have a good effect in the flowability in the dried stated which would be important in some process such as pressing or packaging. This property could also decrease the risk of ultra-fine powder and dust formation during processing. As it was explained before, the silicofluoride compounds of alkaline and earth-alkane elements could have some side-effects on human bodies after inhalation. This mater is important in some industrial application of commercial SSF material such as ceramic or metallurgical industries (Smith, 1985). The presence of the impurity elements such as calcium and oxygen were also characterized by EDAX line scan chemical analysis. Calcium could come from the neutralizing salt during the formation process of the sodium silicofluoride powder in the industrial process. The presence of oxygen could attribute to the presence of the calcium oxide impurity or the presence of surficial absorbed water from atmosphere during test (Jeong et al., 2010).

4. Conclusion

Sodium silicofluoride (Na_2SiF_6) is a well-known raw material candidate in ceramic, metallurgy and chemical industries which is used as a possible fluxing agent or fluorine source in various applications, products and synthesis methods. The understanding of the thermal and microstructural properties of this material could be helpful in the production of some kinds of ceramic materials such as glass-ceramics, enamel and opal products. In this research the thermal behavior (DTA/TGA/DTG) and microstructural properties (SEM/TEM) of a commercial sodium silicofluoride (SSF) powder were investigated. It is revealed the decomposition of the studied commercial sodium silicofluoride powder happens in the temperature range of 432-600 °C associated with an endothermic decomposition reaction and 55.46 wt.% mass loss by heating in air. The morphological studies using scanning electron microscope revealed the granular form of the SSF particles which are consisted from hexagonal shaped prisms and the existence of associated pores. Microstructural investigation using transmission electron microscopy was also proved the availability of the hexagonal shape of the crystallites. Also the EDAX line chemical analysis recorded the distribution of the main constitutional elements of the material as F, Na and Si. However, elements of oxygen and calcium were also detected and attributed to the possible existence of some kinds of impurity oxides such as CaO.

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