

Synthesis of sodium-type fluorophlogopite mica from perlite and diatomite

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Sodium-type fluorophlogopite mica was synthesized by a new and simple method (all-in-one) that consists of mixing diatomite, MgO and NaF, grinding, firing and washing. The solid products were characterized by powder X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR) and scanning electron microscopy (SEM). The results showed that a major phase with lattice spacings of the fluorophlogopite mica ($\text{NaMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) formed was observed at $d = 9.73$ and $d = 3.24$ Å for a single sheet of an interlayer with an anhydrous phase obtained at 1000-1100 °C for 48-72 h. The peak intensity of the sodium-type fluorophlogopite mica became stronger with increasing temperature and time.

Key words: Sodium-type fluorophlogopite, Mica, Perlite, Diatomite, Synthesis.

Introduction

The micas are phyllosilicates and consist of unit layers, each composed of two Si-Al-O tetrahedral sheets between M-O and OH octahedral sheets, where M is usually Al^{3+} , Fe^{2+} , Fe^{3+} , or Mg^{2+} . In the mica layer, octahedra and tetrahedra share corners, and these corners are oxygen atoms. In contrast, two anion sites of the octahedral sheet that are shared only by other octahedra are made of oxygen atoms bound to hydrogen so as to form OH groups, when not comprised of other anions such as F and Cl [1-2]. Micas have a 2 : 1 layer structure for the basic unit layer, with cations in the interlayer separating the basic unit layers. These cations are called interlayer ions and can consist of potassium, sodium, and calcium, with potassium being the more common interlayer ion [3]. Potassium-type fluorophlogopite, $\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$, in which the interlayer cation is K^+ , is a representative synthetic mica. Other micas with smaller interlayer cations are lithium or sodium-type fluorophlogopite ($\text{LiMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$, $\text{NaMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) [4]. In addition, expandable micas, such as $\text{NaMg}_{2.5}\text{Si}_4\text{O}_{10}\text{F}_2$ and $\text{LiMgLiSi}_4\text{O}_{10}\text{F}_2$ [5], and a synthetic mica of a brittle mica composition with highly charged sodium fluorophlogopite mica with a high content of sodium, namely $\text{Na}_4\text{Mg}_6\text{Al}_4\text{Si}_4\text{O}_{20}\text{F}_4$ [6-8], $\text{Na}_3\text{Mg}_{5.5}\text{Al}_2\text{Si}_{5.8}\text{O}_{20}\text{F}_4$ [9-10], and $\text{Na}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{20}\text{F}_4$ [11], have been prepared. The synthetic mica is usually synthesized by using various methods such as hydrothermal synthesis [12], topotactic exchange [13], a sol-gel method [7-8] and solid-state methods [14]. However, the raw materials use natural materials such as talc [5], augite [6], kaolinite [7-11] and fly-ash [15].

Nevertheless, there are a few that are synthesized by using perlite and diatomite. Perlite is a glassy volcanic rock with a chemical composition that is generally equivalent to rhyolite or granite but contains a much higher water content. When it is heated, it will expand to become porous lightweight aggregates according to the rapid loss of water. Perlite was found to be associated with Lamnaria volcanic rocks in Lopburi Province, Thailand [16]. The Lampang Basin (about 1000 km²) is the second largest of its type in northern Thailand. It lies approximately 250 m above sea level, about 70 km directly southeast of Chiang Mai, and is located 500 km north of Bangkok. In the center of the Lampang basin, diatomite is deposited in characteristic small, laterite-capped hills of 10-20 m in height, which protrude from surrounding low-lying rice fields. Along the basin margins, diatomite is usually exposed on down slopes underlying ridges of Quaternary river terrace gravel [17-18]. Diatomite (or diatomaceous earth, or *Kieselguhr*) is a sedimentary rock composed of the skeletons of single-celled diatoms. Moler or moler earth is impure diatomite containing up to 30% clay. Diatoms are microscopic members of the algae family consisting of many thousands of species and are typically 50-100 µm in size. Diatomite is commonly used as a filtering material for water in swimming pools, in beer production, and in the filtration of raw sugar, fats, oils, and pharmaceuticals [19]. The high quality of diatomite in the Lampang Basin has the following compositions: silica (SiO_2) 75-80; alumina (Al_2O_3) 10-12; iron oxide (Fe_2O_3) < 5.0 wt% [18]. Here, we demonstrate the synthesis and characterization of sodium-type fluorophlogopite mica by an economical starting material through a process with a simplified post preparation step. In this method, sodium-type fluorophlogopite is synthesized using an "all-in-one method" in which all components are mixed together and directly crystallized without any pretreatment [20].

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Experimental Procedure

The perlite sample was collected from Lamnaria, Lopburi Province, and the diatomite sample was collected from Ban Keuw, Mae Tha District, Lampang Province, Thailand, for use in the synthesis of fluorophlogopite mica. The all-in-one method was employed in this study for conversion of the natural sample to sodium-type fluorophlogopite mica [19]. The starting materials were original perlite or diatomite (SiO_2 and Al_2O_3 source), MgO , and NaF in near-stoichiometric powder mixtures with reactant ratios of 10 : 1 : 1 : 3.5. The mixture was thoroughly homogenized using a mortar and pestle and transferred to a platinum crucible. Samples were prepared at temperatures ranging from 1000 to 1100 °C for 48-72 h in air using a programmed furnace. After cooling, the solid was crushed and washed with deionized water several times to remove excess fluoride. Any remaining impurity phase, such as soluble fluoride salts, were removed with repeated washing using a saturated boric solution, followed by three washings with 1 M NaCl solution to saturate all exchange sites with Na ions. The mica thus prepared was finally washed with deionized water, dried at 105 °C in an oven for 24 h and stored in desiccators over silica gel at room temperature (Fig. 1). Powder X-ray (XRD) patterns were examined using a Phillips PW 1803 X'pert system X-ray diffractometer generator operating at 45 kV with a 40-mA $\text{Cu K}\alpha$ radiation source at a wavelength of 1.5406 Å. The samples were run from 5° to 50° 2θ , with a step size of 0.02° 2θ and a step time

of 2 seconds or 1 second. A JSM-5410LV scanning electron microscope (SEM) with INCA software by Oxford for energy dispersive X-ray spectroscopy was used to estimate the elemental composition of different regions of the product. To prepare for the observation, the sample was placed on a brass stub sample holder using carbon tape. Then, the sample was dried using infrared light. After that, the sample was coated with a layer of gold approximately 20-25 Å thick using a Balzer sputtering coater to make them conductive. The micrographs were recorded with an acceleration voltage of 10 kV and at 2000-5000x magnification. Fourier transform infrared spectrometry (FT-IR) was used to study structural features. The instrument used for this analysis was a Shimadzu model 8900 with the KBr pellet technique. Infrared spectroscopy studies were performed for the mid-infrared region (from 1800 to 400 cm^{-1}) where vibrational and rotation bands are observed. The spectra were obtained using an average of 20 scans with 8 cm^{-1} resolution.

Results and Discussion

The chemical compositions of perlite and diatomite in the form of stable oxides are shown in Table 1. The major component was SiO_2 with 34.30 wt% for perlite and 72.40 wt% for diatomite, respectively, along with other inorganic oxides including Al_2O_3 , CaO , Fe_2O_3 , TiO_2 , MgO , K_2O and Na_2O . The silica and alumina were sufficient to use as a source for the synthesis of sodium-type fluorophlogopite mica. XRD patterns of the synthetic mica specimens are shown in Figs. 2 and 3. For the synthetic sodium-type fluorophlogopite specimen from natural diatomite, some impurities and neighborite were observed at 1000 °C. Although impurities disappeared at 1100 °C, the small peaks of an unknown substance remained, and neighborite was observed. The peak intensity of the mica became stronger with an increase in duration time to 72 h. The lattice spacing of the mica formed at 1000-1100 °C corresponded to those of sodium-type fluorophlogopite ($\text{NaMg}_3\text{AlSi}_3\text{O}_{10}\text{F}_2$) [21], as described in JCPDS card no. 25-0842 and observed at $d = 9.73$ and 3.24 Å, which were assigned to the (001) and (003) reflections of a single sheet of an interlayer with an anhydrous phase. The small peaks observed around $d = 3.83$, 2.71 and/or 1.91-1.94 Å are assigned to the (110), (112), and (220) reflections of the sodium magnesium fluoride or neighborite (NaMgF_3 , JCPDS card no. 82-1224). Many different phases can be seen in the XRD patterns. Regarding the XRD pattern of the solid preparation procedure, the product of a reaction with perlite

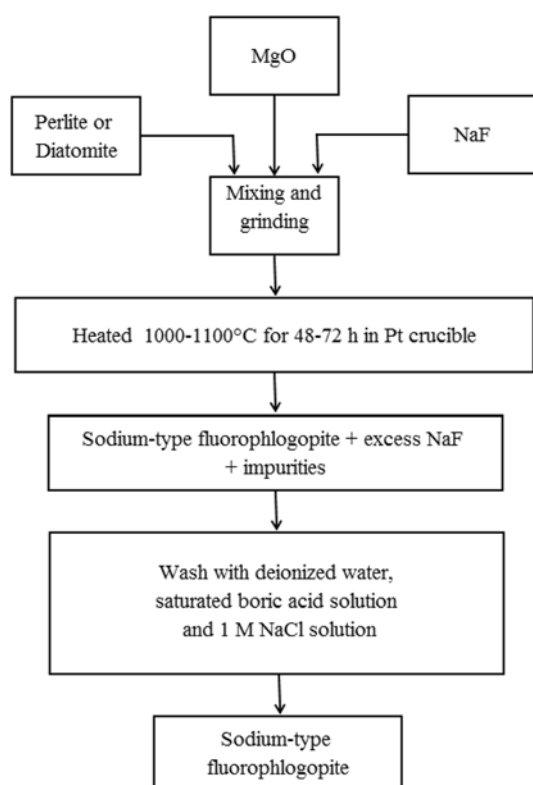


Fig. 1. Flow chart for the synthesis of sodium-type fluorophlogopite mica.

Table 1. Chemical compositions of perlite and diatomite

Sample	Chemical compositions (wt%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	LOI
Perlite	34.30	8.10	1.69	0.25	24.80	1.96	1.74	0.89	21.40
Diatomite	72.40	12.50	5.80	0.40	0.23	0.52	1.34	0.31	6.20

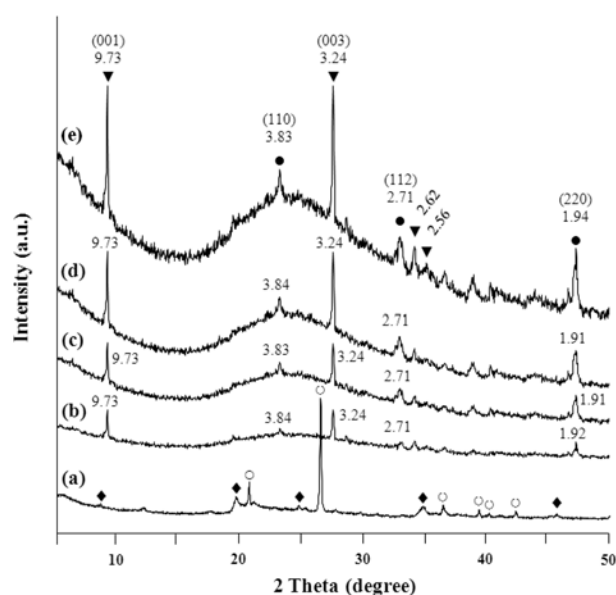


Fig. 2. XRD pattern of (a) diatomite and synthetic sodium fluorophlogopite specimen at (b) 1000 °C for 48 h, (c) 1000 °C for 72 h, (d) 1100 °C for 48 h, and (e) 1100 °C for 72 h. (▼): mica, (●): neighborite, (◆): muscovite, (○): quartz, no-mark: unknown.

is shown in Fig. 3. The XRD pattern revealed that perlite was not converted to sodium-type fluorophlogopite, indicating that a crystalline phase together with impurity phases were observed at 1100 °C for 48 and 72 h. On the other hand, when perlite was used as a starting material instead of silica and alumina sources, it was difficult to synthesize. In particular, the high content of calcium oxide in perlite formed augite, akermanite, and wallastonite-1A phases

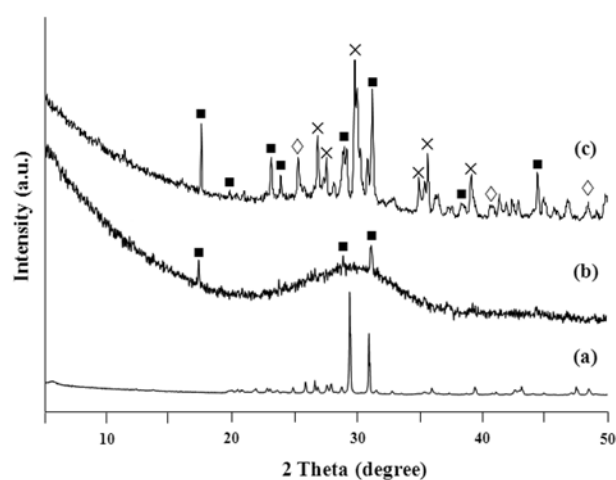


Fig. 3. XRD pattern of natural perlite (a) and synthetic phase specimen at (b) 1100 °C for 48 h and (c) 1100 °C for 72 h. (×): augite, (■): akermanite and (◇): wallastonite-1A.

(JCPDS card no. 78-1391, 72-2127 and 10-0487, respectively). However, this method aimed to synthesize sodium-type fluorophlogopite mica, but peaks attributed to impurities still remained. Thus, the “all-in-one” method using diatomite to synthesize sodium-type fluorophlogopite is expected to be cost effective for commercial production compared to the general method, which uses fine chemicals. Diatomite is a cheap silica and alumina source, while fine chemicals are more costly.

FT-IR characterization

The IR studies of natural diatomite are shown in Fig. 4(A). Because the major composition of the diatomite sample

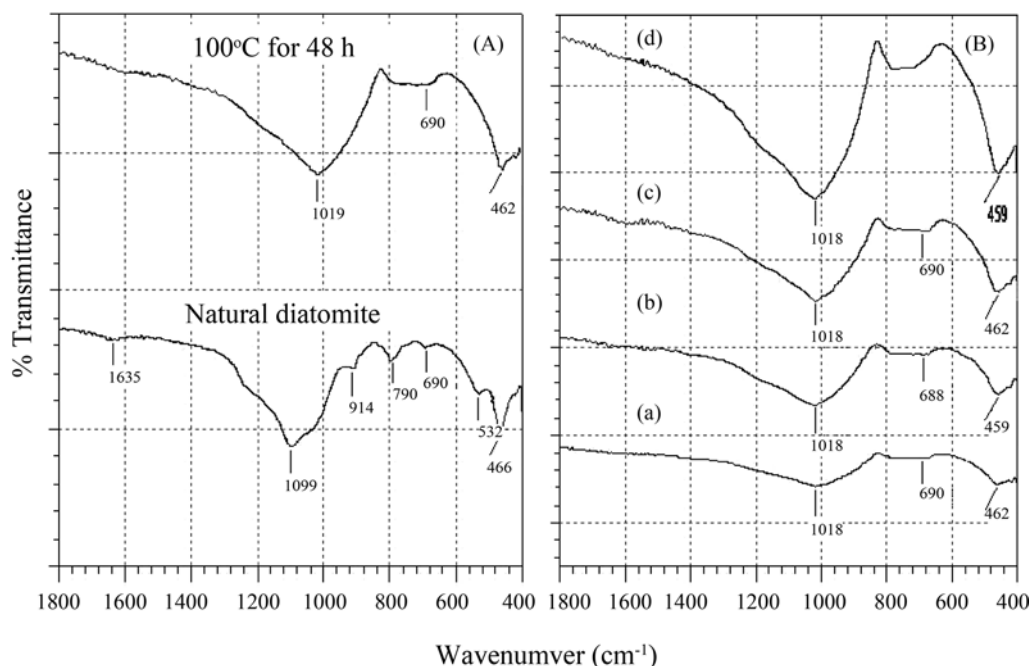


Fig. 4. IR transmission spectra for (A) comparison of synthetic mica and natural diatomite and (B) a sodium-type fluorophlogopite specimen at (a) 1000 °C for 48 h, (b) 1000 °C for 72 h, (c) 1100 °C for 48 h, and (d) 1100 °C for 72 h.

was silicon oxide, the IR spectra exhibit a series of transmission bands, as expected. The FT-IR spectral band intensities of the natural diatomite were at 1635, 1099, 914, 790, 690, 532 and 466 cm^{-1} . The band at 1635 is assigned to the bending vibration of adsorbed water. In the low wave numbers region, there were up to 6 characteristic bands of natural diatomite, and the bands at 1099 were mainly attributed to siloxane (Si-O-Si) stretching of amorphous silica. The band at 533 was due to Si-O-Al bending. The bands at 790 cm^{-1} correspond to an intertetrahedral Si-O-Si bending vibration, while the 690 and 466 cm^{-1} bands were due to O-Si-O bending, and the 914 cm^{-1} band may be due to Si-OH stretching and Al-Al-OH bending [21-23]. The infrared spectra of quartz and muscovite disappeared with conversion from natural diatomite to sodium-type fluorophlogopite. The lower part of the spectra in the range of 1200-400 cm^{-1} can be assigned to lattice vibrations of the (Si,Al)-O and Mg-O of fluorophlogopite [6]. The band at 1023 cm^{-1} may be assigned to Si-O stretching in the Na 2 : 1 layer [5]; however, in this study it was shifted to 1018 cm^{-1} . The bands at 690 cm^{-1} are attributed to the symmetric Si-O-Si stretching vibration, and the bands at 462 and 459 cm^{-1} indicate Si-O bending [24]. Bands at 690 and 462 cm^{-1} appeared at temperatures of 1000 and 1100 $^{\circ}\text{C}$ for 48 h, and wave numbers of 686 and 459 appeared for a duration of 72 h. The infrared spectra of the sodium-type fluorophlogopite specimen under all synthesis conditions were also recorded, as shown in Fig. 4(B).

Morphological and elemental analysis

Scanning electron microscopy is one of the most versatile and useful methods to study crystal morphology and crystal size. The morphology of the natural diatomite shown in Fig. 5 is typical, showing the dominant *A. granulata* species. The natural diatomite had an average particle size of 9 μm . The SEM images of sodium-type fluorophlogopite synthesized in a Pt crucible at 1000 and 1100 $^{\circ}\text{C}$ for 72 h are shown in Figs. 6 and 7. The SEM images of the two conditions obtained from scanning electron microscopy suggest that the crystal size of the synthesized materials

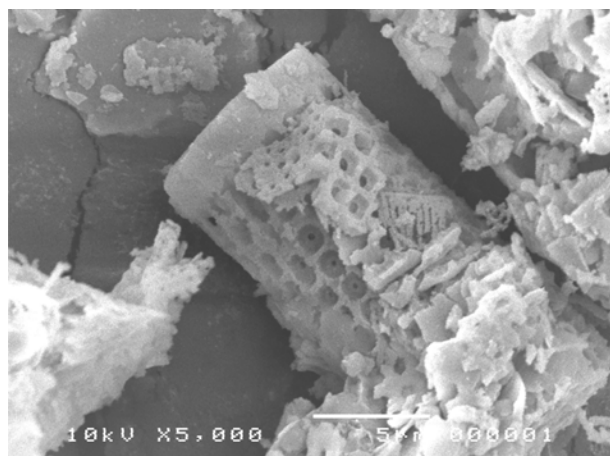


Fig. 5. SEM micrograph of diatomite sample at 10 kV.

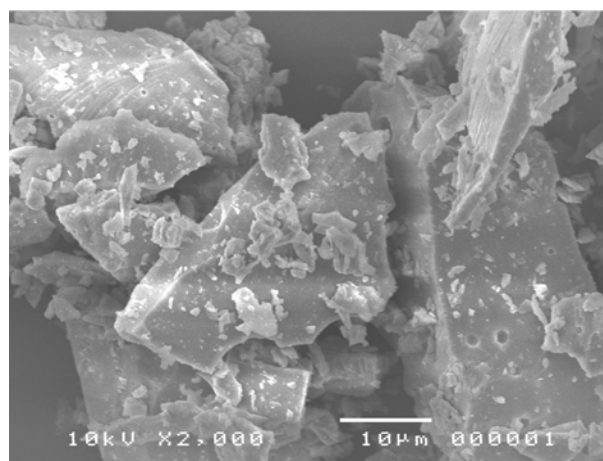


Fig. 6. SEM image of sodium-type fluorophlogopite synthesized from diatomite in a Pt crucible at 1000 $^{\circ}\text{C}$ for 72 h.

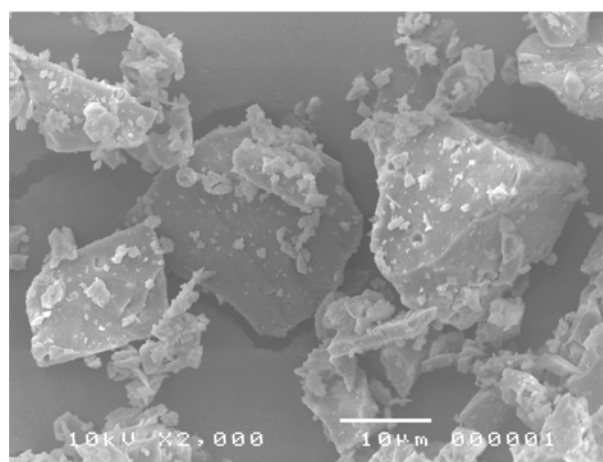


Fig. 7. SEM image of sodium-type fluorophlogopite synthesized from diatomite in a Pt crucible at 1100 $^{\circ}\text{C}$ for 72 h.

is in the range of 10-40 μm . The particles were uniform in size, and some crystals apparently fused together to form agglomerates. The morphologies indicative of diatoms of natural diatomite were not found, which indicates nearly complete conversion of natural diatomite to sodium-type fluorophlogopite. The chemical composition of the synthesized sodium-type fluorophlogopite was checked by elemental analysis for O, F, Na, Mg, Al and Si using energy dispersive spectrometry (EDS) analysis. The estimated values (Figs. 8, and 9) agree well with these elements based on their crystal structure.

Conclusions

Sodium-type fluorophlogopite mica was synthesized using diatomite, MgO and NaF at 1000 and 1100 $^{\circ}\text{C}$ for 48 and 72 h in air using a programmable furnace. This mica seems to be formed by the transformation from natural diatomite. Diatomite was found to be a good aluminosilicate source in the synthesis of the sodium-type fluorophlogopite mica. The method consisted of just four processes, which

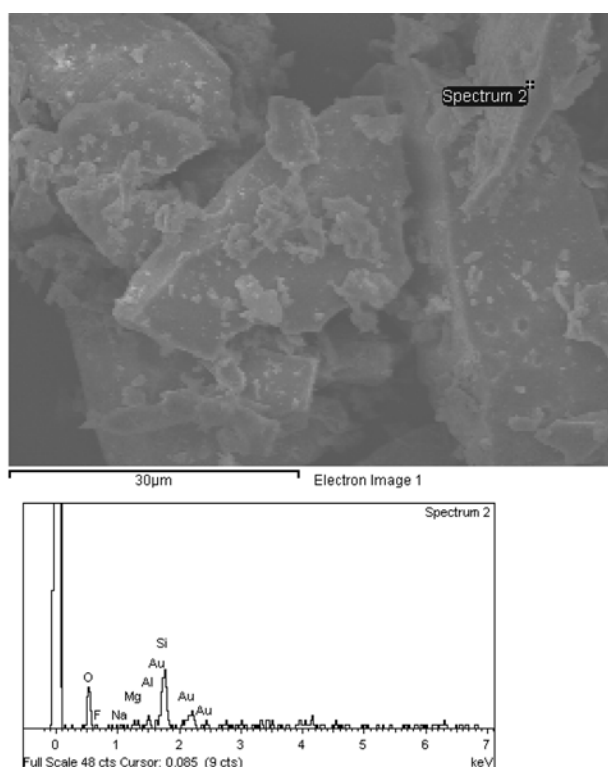


Fig. 8. EDS spectrum of sodium-type fluorophlogopite synthesized from diatomite in a Pt crucible at 1000 °C for 72 h.

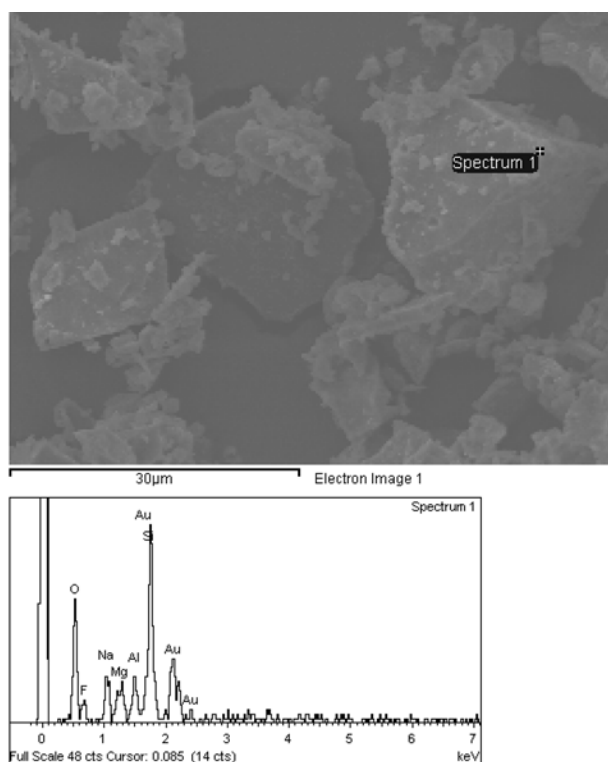


Fig. 9. EDS spectrum of sodium-type fluorophlogopite synthesized from diatomite in a Pt crucible at 1100 °C for 72 h.

were mixing, grinding, firing and washing. The synthesis of sodium-type fluorophlogopite mica using diatomite

is expected to be cost-effective because this material is an inexpensive source of Si and Al. However, future studies are needed for further optimization of the synthesis conditions to obtain pure sodium-type fluorophlogopite mica.

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