Synthesis of Fluorophlogopite Using Solid-State Reaction Techniques

by

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(ABSTRACT)

A commercial solid-state batch process for the manufacturing of synthetic fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) mica powder was evaluated and standardized. The minimum firing temperature and time for this process was determined to be 1000°C for 10 hours to both ensure the complete reaction of the raw materials and to limit the decomposition of the mica into secondary phases that occurs during overfiring. The addition of an excess amount of the fluoride K_2SiF_6 to compensate for the loss of fluorine that occurs during firing was found to increase the formation of fluorophlogopite. Additionally, enclosing the material within closed containers also limits the loss of fluorine from the batch. The practice of pressing the raw material blend into cakes before firing was found to have no effect on the formation of fluorophlogopite and is, therefore, an unnecessary processing step. Finally, a quality control testing procedure that will be used in industry was developed to determine the amount of mica formed during a given heat.

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1. Introduction

Mica is an abundant and common mineral long valued for its intrinsic properties, enabling its use in an essentially raw form without extensive processing. Along with its characteristic cleavability, flexibility, and transparency, mica is also known for its electrical properties, namely its high dielectric strength. The combination of these properties, plus the fact that it is an inexpensive mineral, makes mica a versatile material with uses ranging from structural to electrical applications. Because of its electrical and insulating properties, mica was at one time used extensively for electrical applications, such as in radio tubes, generators, and condensers. But since the development of other electronic materials, the use of mica in these applications has long been obsolete. Since then, other uses have been developed to take advantage of mica's unique characteristics. Present day applications include blending the mica powder with organic powders to form polymer-matrix composites for structural, electrical, and wear-resistant applications.

Despite the abundance of the inexpensive natural micas, synthetic micas are currently being processed and used as substitutes. These synthetic micas, particularly fluorine micas, are often preferred because their properties are

considered superior to the natural micas. One of these synthetic micas is fluorophlogopite, $KMg_3AlSi_3O_{10}F_2$, the synthetic form of the magnesium mica phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$. Fluorophlogopite is known for its high thermal stability and chemical uniformity, characteristics atypical of natural phlogopite. This chemical uniformity allows the possibility of controlling and modifying the properties of the end mica product and the materials made with them. Because of these and other advantages, synthetic micas are currently processed and used as a preferred substitute for natural micas.

There are two primary methods used in processing synthetic fluorine micas on a production-scale. The first method involves the melting of the raw materials at high temperatures (> 1350°C), allowing time to complete a reaction to form the mica, and slowly cooling the melt to produce sheet mica. This sheet mica is broken down into flakes with a minimum thickness of 0.018 cm and a minimum surface area of 2.54 cm^2.[1, 2] The primary applications of high quality sheet mica include spacers and insulators in vacuum tubes, insulating washers for electronic equipment, optical filters, and transmitting and receiving capacitors.

Solid-state processing, on the other hand, occurs at lower temperatures (< 1150°C) and is primarily used to produce a fine mica powder (< 10.0 μm). Mica produced from this method is chiefly used in gypsum plasterboard cement as a filler and extender that provides a smooth consistency and resists cracking. Other applications include pigment extenders for paints, inert fillers and surface coatings for roofing and asphalt shingles, and reinforcing agents in polymer composites.[2]

Difficulties in producing a consistent fluorophlogopite product were encountered using a particular solid-state processing method. The goal of this research was to evaluate and optimize a commercial batch synthesis of fluorophlogopite mica using solid-state reaction techniques. Methods that were used to evaluate the composition and crystallinity of the final product include X-ray diffraction (XRD) analysis, a fluoride ion selectivity test, mica solubility testing, and particle size analysis (PSA). To get a better understanding of fluorophlogopite processing, a complete evaluation of the process was performed in the following four areas:

1) Raw material composition and blending
2) Material compaction and pressing
3) Mica firing
4) Milling and particle size analysis.

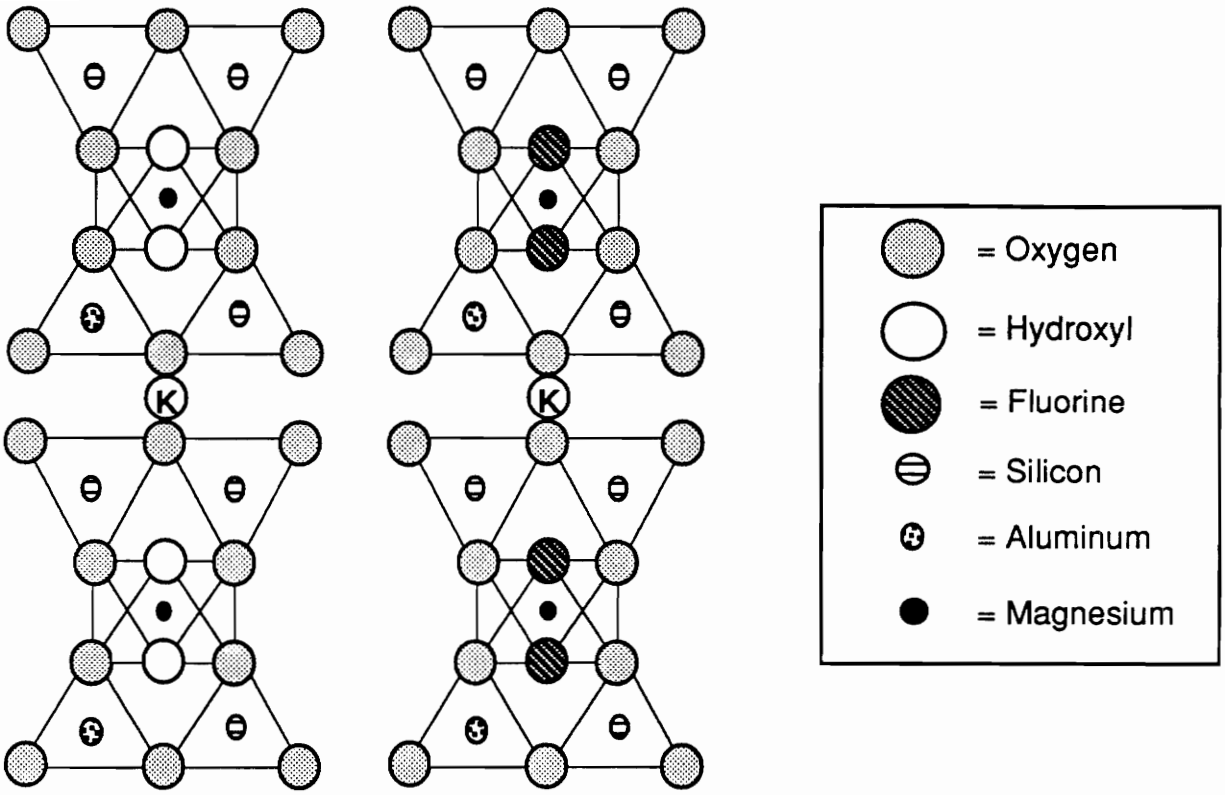
Both bench-scale and production-scale experiments were conducted in these areas to determine the effects of processing variables, such as raw material composition and firing time and temperature, on the composition of the final product. These results were then used to improve the current batch processing technique by making procedural changes while minimizing changes in the equipment used. Finally, a quality control test was developed and introduced as a production-scale procedure which will be used to determine the composition of the final product.

2. Literature Review

2.1 Synthetic Fluorophlogopite

Naturally occurring micas are hydrated alumino-silicate minerals that have similar crystal structures but varying chemical compositions. Among the most common micas is the magnesium mica, phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$. Figure 1 illustrates the similar crystal structures of both natural and synthetic phlogopite. The basic structural unit consists of a layer of three sheets, two tetrahedrally coordinated alumino-silicate ($AlSi_3O_{10}$) sheets surrounding an octahedrally coordinated brucite ($Mg(OH)_2$) sheet, producing a single layer of mica. This stacking arrangement is repeated indefinitely, with potassium ions separating each layer to form layers of mica.[3]

The two primary crystalline structures of fluorophlogopite are monoclinic and hexagonal forms.[4, 5] Examination of X-ray diffraction data reveals small, yet distinct, differences in the peak intensities of the two forms. A close examination of X-ray



a. Natural phlogopite

b. Synthetic phlogopite

Figure 1. Schematic diagrams of structures of (a) natural and (b) synthetic phlogopite

diffraction patterns of samples produced from both the bench-scale and production-scale heats have indicated that the monoclinic form is prevalent.

The unit layers of monoclinic fluorophlogopite extend indefinitely in the **a** and **b** directions and are stacked in the **c** direction. The K^+ cation is in twelvefold coordination, with its single charge distributed evenly to the 12 neighboring oxygens, six from each adjacent fluorophlogopite layer. Both natural and synthetic phlogopite are examples of trioctahedral micas, where all of the possible octahedral positions within the structure are filled. Ideally, the octahedral positions of both natural and synthetic phlogopite are occupied primarily by Mg^{++}, as shown in Figure 1.[6]

Cleavage of both normal sheet and powdered synthetic micas occurs between the layers, where the layers are separated by the K^+ cations. This occurs because K^+ has a small charge of 1, and the existence of a weak bond between the K^+ ion and the 12 neighboring $O^=$ anions.[6]

Fluorophlogopite, $KMg_3AlSi_3O_{10}F_2$, is a form of synthetic mica that has superior dielectric and thermal properties compared to natural phlogopite. Properties of natural phlogopite and synthetic fluorophlogopite are shown in Table 1.[7] Synthetic fluorophlogopite not only has the high dielectric strength and relatively low cost of natural phlogopite, but it also has a higher decomposition temperature and is more chemically uniform. For example, its thermal stability permits hot-pressing of fluorophlogopite into various forms, such as sheets and blocks, at temperatures above which natural phlogopite decomposes (900 - 1000°C).[6, 7] The newly pressed product is a soft, machinable electrical insulator that can be machined

Table 1. Physical and electrical properties of natural phlogopite vs. synthetic fluorophlogopite

		Synthetic fluorophlogopite	Natural phlogopite
Density	(g/cm^3)	2.88	2.6-3.2
Crystal structure		Monoclinic	Monoclinic
Maximum constant use temperature before decomposition	(°C)	1100	850
Melting point	(°C)	1387	Decomposes
Tensile strength	(ksi)	45-52	37-43
Modulus of elasticity	(psi)	25×10^6	25×10^6
Dielectric strength	(kV/mm)	185-238	125-281
Dielectric coefficient		5.6-6.3	5.0-7.0

to close tolerances without concern for shrinkage corrections, especially when continuous use at elevated temperatures (> 800°C) is desired.[8]

Figure 1 shows that the main difference in the crystal structures of natural and synthetic phlogopites is the substitution of the fluoride ion (F^-) in fluorophlogopite for the hydroxyl ion (OH^-) found in natural phlogopite. This direct substitution occurs rather easily because the ionic radii of F^- (1.33 A) and OH^- (1.40 A) are approximately equal. In fact, the substitution of F^- for OH^- occurs so frequently that it is not uncommon for natural phlogopite to contain up to 3% fluorine.[9]

The higher thermal stability of synthetic phlogopite can be attributed to the substitution of F^- for the OH^- found in natural phlogopite. Natural phlogopite decomposes by releasing OH^-, resulting in hydrolysis when heated to relatively low temperatures (300°C). On the other hand, fluorophlogopite is stable until its softening temperature, 1100 - 1200°C, eventually melting at 1350°C, where volatilization of gaseous fluorides, such as SiF_4, KF, and HF, occurs.[10] One method of forming a volatile fluoride occurs by combining water vapor with the free fluorine emitted during a firing within a furnace, producing HF gas. Water can be present in many forms, including the moisture absorbed into the batch of raw materials or simply a moist atmosphere within the furnace at firing conditions.[10, 11]

The formation of normal synthetic fluorophlogopite through solid-state reactions has been studied thoroughly by Beaver, et. al .[12] A typical stoichiometric

reaction of normal synthetic fluorophlogopite is shown below:

$$2K_2SiF_6 + K_2CO_3 + 3Al_2O_3 + 18MgO + 16SiO_2 \text{ ---> } 6KMg_3AlSi_3O_{10}F_2 + CO_2$$

Reactions including excess amounts of fluorine proposed by Beaver, et al., are given below:

<u>for 10 mol% excess K_2SiF_6:</u>

$$11K_2SiF_6 + 4K_2CO_3 + 15Al_2O_3 + 90MgO + 79SiO_2$$

$$\xrightarrow[1\ 1/2\ O_2]{} 30KMg_3AlSi_3O_{10}F_{2.2} + 4CO_2$$

<u>for 25 mol% excess K_2SiF_6:</u>

$$5K_2SiF_6 + K_2CO_3 + 6Al_2O_3 + 36MgO + 31SiO_2$$

$$\xrightarrow[1\ 1/2\ O_2]{} 12KMg_3AlSi_3O_{10}F_{2.5} + CO_2$$

It is apparent from these reactions that under ideal conditions, CO_2 is the only gaseous phase present; however, this is not always the case. For example, some of the raw materials used to produce fluorophlogopite are hygroscopic, most notably MgO and K_2CO_3.[11] The presence of excess moisture within the system, either absorbed by the raw materials or in the atmosphere inside the furnace, can lead to defluorination of the heated batch through a combination of hydrolysis and decomposition of the K_2SiF_6, forming gaseous HF.[10, 11, 12] Precautions are therefore taken to limit the amount of moisture in any given batch. They include using

materials enclosed in moisture-resistant packaging and limiting the exposure of the raw materials to excess moisture within the surroundings by blending the raw materials immediately before firing.

Figure 2 shows the differential thermal analysis (DTA) data obtained for the natural and synthetic phlogopites. The presence of endothermic peak at a relatively low temperature (900 - 950°C) represents the dehydroxylation and decomposition of the natural phlogopite. However, the fluorophlogopite curve is essentially straight, lacking any endothermic or exothermic peaks until its melting temperature, 1350°C. Because F^- is substituted for OH^- in fluorophlogopite, the mineral undergoes no dehydroxylation. The absence of the peaks illustrates the stability of synthetic mica through a large temperature range, indicating the absence of both phase changes and material decomposition until temperatures approaching the melting point are reached.

2.2 Role of Fluorides in Batch Reactions

Early work at the U.S. Bureau of Mines by Eitel, et al.,[10] was done to study the potential commercial processing methods of a synthetic mica that could be used as a substitute for strategic varieties of sheet mica. During the course of the study, the effects of various fluorides on batch reactions was examined. Numerous fluorides that were possible candidates to synthesize fluorophlogopite were studied. To be considered acceptable, a fluoride should be:

1) commercially available in industrial quantities

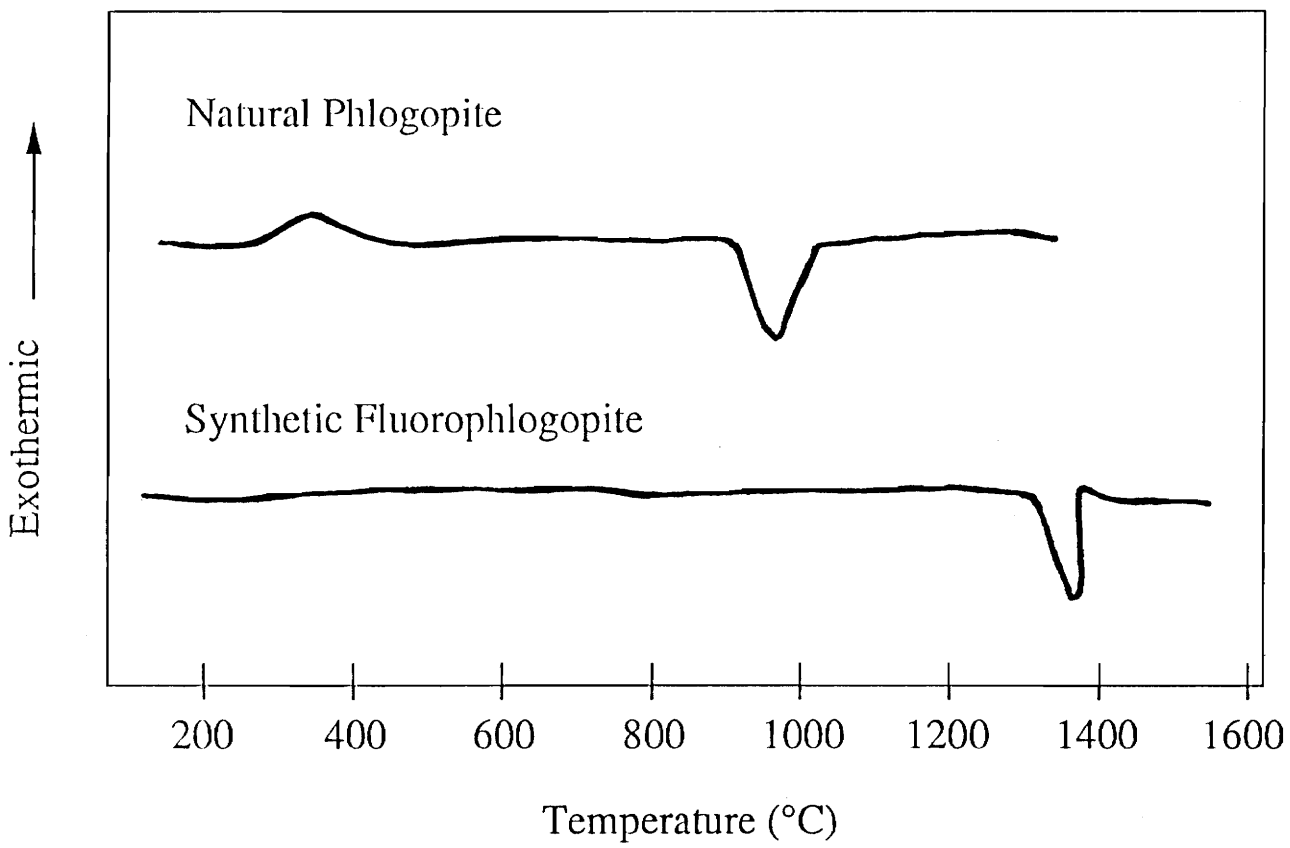


Figure 2. DTA curves for natural and synthetic phlogopite

2) relatively free from contamination by compounds that would inhibit the properties of fluorophlogopite, such as soda, lime and iron

3) non-hygroscopic, or should become anhydrous before or during processing

4) relatively inexpensive.

Based on these requirements, the following fluorides were studied:

KF, MgF_2, $KMgF_3$, AlF_3-H_2O, K_2SiF_6, $MgSiF_6$-$6H_2O$, K_3AlF_6 and K_2AlF_5.

Some fluorides, such as MgF_2, K_3AlF_6 and K_2AlF_5, were considered too expensive for production-scale use, while others such as $MgSiF_6$-$6H_2O$, AlF_3-H_2O and KF contained significant amounts of moisture. For the purposes of solid-state reactions, K_2SiF_6 was considered to be the best fluoride because of its high reactivity within the solid-state reaction temperature range, high purity, low cost and wide availability. Also, K_2SiF_6 is preferred because it is an anhydrous and non-hygroscopic material.[11]

Studies were also done to determine the reaction of these fluorides with the oxides within the raw material batch used to produce fluorophlogopite. These oxides, Al_2O_3, MgO, and SiO_2, were tested with the fluorides in binary systems in order to study them in greater detail. Again, K_2SiF_6 was determined to be satisfactory because it readily reacts with these oxides at the fluorophlogopite solid-state formation temperatures (500 - 1200°C).[10]

Potassium silicofluoride is a stable compound at room temperature that decomposes to form volatile fluorides, KF and SiF_4, at low firing temperatures ($\geq$ 500°C).[10] Eitel, et al., also reported the vapor pressures of K_2SiF_6, which are shown

in Table 2, indicating that gaseous SiF_4 is readily available at temperatures best suited for solid-state formation of fluorophlogopite, between 500 and 1200°C.

In analyzing the effects of fluorine in mica batch reactions, Eitel, et al., found that a small excess amount of fluoride in a given batch should be used to compensate for the loss of fluoride due to the volatilization in solid-state reactions; otherwise, decomposition products such as spinel ($MgAl_2O_4$), forsterite (Mg_2SiO_4) and leucite ($KAlSi_2O_6$) can form from a significant loss of fluorine.[12] It should be noted that the use of K_2SiF_6 was recommended over other fluorides, such as MgF_2 and K_3AlF_6, because of the formation of higher concentrations of fluorophlogopite.

Problems exist, however, when using an excess amount of fluorine within a batch to compensate for the loss of fluorine during heating. From a materials point of view, an excess amount of fluorine in a batch can result in the formation of fluorides such as MgF_2, resulting in the reduction of electrical properties and the thermal stability of the end product.[12] Formation of vitreous material can also occur, which tends to reduce the machinability of the product. There are also some concerns about how excessive amounts of fluorine within the furnace may result in the corrosion of the refractory lining and the exhaust system of the furnace, thereby effectively increasing the cost in processing fluorophlogopite.

2.3 Methods in Evaluating Fluorophlogopite

There are two types of analyses necessary to evaluate fluorophlogopite. The first type determines the phases that are formed during the firing of raw materials.

Table 2. Vapor pressure of K_2SiF_6 versus temperature, as reported by Eitel, et al.

T (°C)	P (atm)
975.1	0.0308
1026.1	0.0439
1076.1	0.0968
1110.1	0.1780
1125.1	0.2423
1147.1	0.5293
1180.1	1.5120

Methods in this category include X-ray diffraction (XRD) analysis and the use of an ion selective electrode test. The second type, particle size analysis (PSA), determines the average particle size and distribution in the milled final product. This is necessary because manufacturer's specifications must be met concerning the use of specific mica particle sizes in various polymer-matrix composites, the primary use of fluorophlogopite in this project.

One method used to determine the phases present in the fluorophlogopite samples prepared on both bench-scale and production-scale conditions is through XRD analysis. The advantage of this method is that it can be used to accurately identify the phases formed in the final product. These phases may include fluorophlogopite, raw materials used in processing, and secondary fluorine-deficient phases formed during firing, such as spinel, forsterite, and leucite.[13]

An additional method that can effectively determine the amount of fluorophlogopite in the final product is the Fluoride Ion Selectivity Test. A fluoride ion selective electrode, connected to a millivolt meter, is placed in a solution containing a fluoride compound (such as fluorophlogopite) and is used to determine the electric potential of the solution. From this electric potential, the fluoride ion concentration in the solution can be calculated.[14, 15, 16, 17] Since fluorophlogopite is the only phase in which F^- is present, the resulting fluorophlogopite content in the final product can then be calculated. The main advantage of this procedure is that it can accurately detect fluorine values ranging from 44 to 51800 ppm.[15] However, caution should be used for samples that contain more than one fluoride. The

fluorine concentration can be calculated using this method, but it would be difficult to determine the amounts of each fluoride present in the final product.

The particle size of the mica product is important in establishing the mechanical, electrical, and thermal properties of a composite material using fluorophlogopite as its reinforcement material. Equipment used in determining the average particle size of the milled product include the Fisher Sub-Sieve Sizer (FSSS) and the Shimadzu Particle Size Analyzer (PSA).

The FSSS is a device that uses a relatively simple procedure, and is used primarily in industry. It uses a method based on the air permeability through a compacted fluorophlogopite sample of a given mass, thereby indicating the theoretical particle size. The Shimadzu PSA employs a disk-centrifuge configuration. With this method, a powder sample is dispersed in an aqueous solution containing a surfactant, such as sodium pyrophosphate (commonly known as Calgon), and placed in a spinning disk. The surfactant allows the dispersion of the fluorophlogopite particles, giving a more accurate particle size distribution. A light source is placed at a given distance from the outer edge of the disk, which then detects the sizes and number of the particles as they settle to the bottom of the quartz chamber. Settling of the smaller particles is enhanced by the gradual acceleration of the disk. The particle size distribution is then determined through the use of Stokes' Law.[18]

3. Experimental Procedure

According to standardized fluorophlogopite production procedures,[12] the following procedure was used initially in the batch-processing of fluorophlogopite. The compounds used to produce fluorophlogopite through solid-state methods are as follows (expressed in weight percentages): 11.90% Al_2O_3, 5.38% K_2CO_3, 17.13% K_2SiF_6, 28.22% MgO, and 37.37% SiO_2. To produce fluorophlogopite, ingredients in the desired stoichiometric proportions are blended to form what is defined as the **raw material blend**, and cold-pressed into 13-lb cakes using a pressure of 5000 psi. The cakes are placed in cordierite saggers and stacked onto a furnace cart before being loaded into a furnace, as shown in Figure 3. The load is fired for 17 hours at 1200°C to allow reaction of the raw materials. The cakes are then removed from the furnace, allowed to cool to room temperature, and coarsely ground and milled to the desired particle size (2.0 - 4.0 μm).

The following experiments, both bench-scale and production-scale, follow the above basic procedure, with modifications noted when necessary.

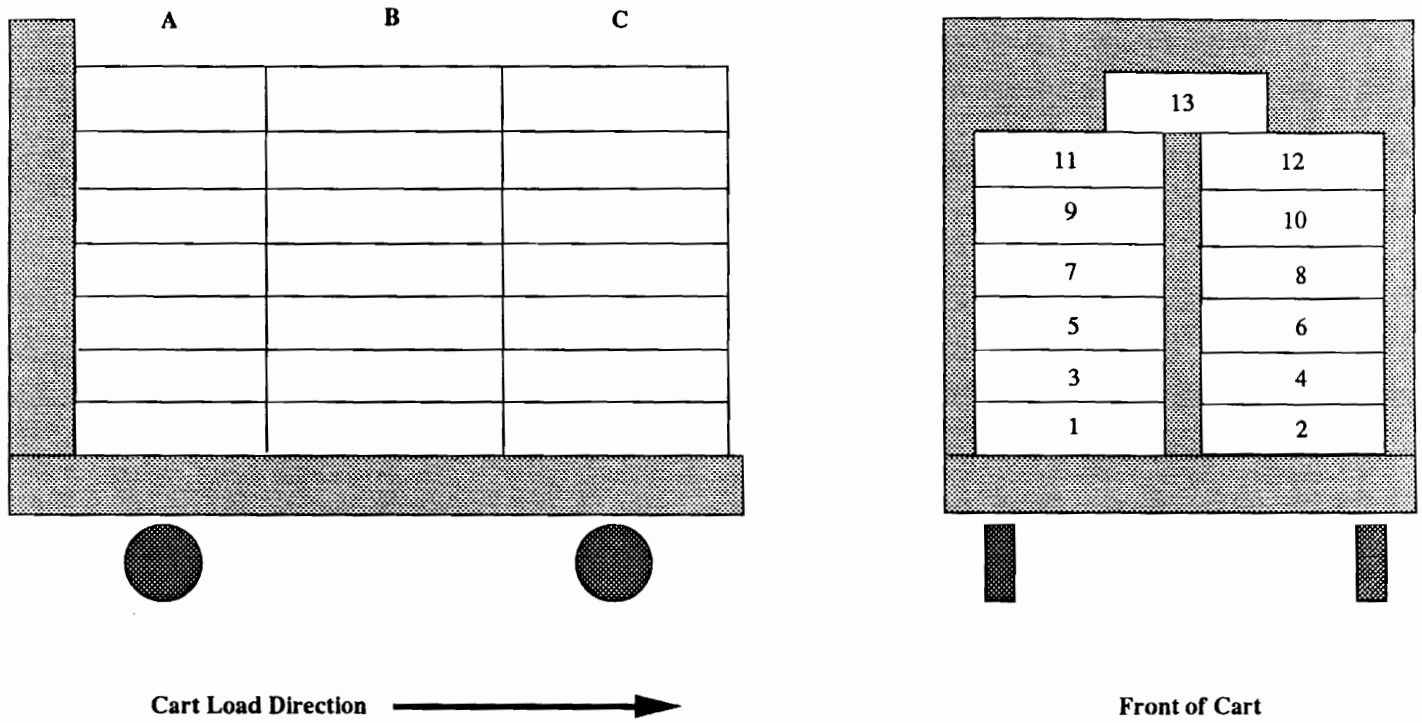


Figure 3. Location of cordierite saggers on a cart for production-scale furnace.

3.1 Establishing Minimum Firing Times and Temperatures

Bench-scale experiments were conducted to determine the minimum firing time and temperature at which the raw materials react to form fluorophlogopite. Samples having stoichiometric compositions were weighed to 2.00 g and pressed into pellets with pre-firing dimensions of 1.25 cm in diameter and 0.50 cm in thickness. In pressing the raw material, a pressure of 5000 psi was used to form the pellets. Binding agents, such as organic binders or water, were not used. Samples were fired at 850-1000°C, with firing times ranging from two to 14 hours. XRD analysis was conducted to determine the phases present within each sample. The firing temperature of each set of samples was determined using a Type S (Pt / Pt-10% Rh) thermocouple placed directly next to the samples.

3.2 Composition of Pre-fired Blend

Bench-scale experiments were also conducted to determine the effect of the amount of fluorine in the raw material pre-fire blend on the formation of fluorophlogopite. Compositions of the blends were designed to test three types of blends: stoichiometric composition, and compositions containing 10% and 20% excess K_2SiF_6. The composition of the blends are given as follows (expressed in weight percentages):

Excess K_2SiF_6	Al_2O_3	K_2CO_3	K_2SiF_6	MgO	SiO_2
stoichiometric	11.90	5.38	17.13	28.22	37.37
10% excess	11.70	5.28	18.52	27.74	36.75
20% excess	11.50	5.20	19.88	27.29	36.14

Each sample was prepared in the following manner: a 2.00 g sample was weighed and pressed into pellets (1.25 cm diameter and 0.50 cm thickness) using a pressure of 5000 psi. Again, no binding agent was used. Two experiments were conducted on these samples. In the first experiment samples were fired in a furnace set at a constant temperature (1050°C) with the firing times varying from 5 to 20 hours. In the second experiment, pellets were prepared as above, but were fired for 13 and 15 hours at temperatures ranging from 1000 - 1250°C. Constant heating and cooling rates were used in all bench-scale experiments in order to obtain consistent results. Heating rates (200°C/h) and cooling rates (100°C/h) were designed to duplicate the rates in production-scale furnaces. In each of the above experiments, a Type S thermocouple was placed directly adjacent to the samples to accurately determine firing times and both heating and cooling rates. XRD analysis was again used on finely ground powders to determine the amount of fluorophlogopite and the possible presence of other secondary phases.

3.3 Sample Evaluation

A Phillips X-ray Diffractometer Model PW 1840 was used to scan powder samples produced from bench-scale and production-scale heats. The X-ray tube operated at a voltage of 40 kV and a 30 mA current for all tests. Cu Kα radiation was used.

Bench-scale samples were prepared for XRD analysis by finely grinding the fired pellets with an Al_2O_3 mortar and pestle and mounting the powder on an

aluminum sample holder. Production-scale samples were prepared by taking a representative sample from each region of the furnace, grinding and mounting each sample as above. The powdered samples were scanned in a 2 range of 7° to 70° to detect the presence of fluorophlogopite, unreacted raw materials, and secondary phases, such as spinel, leucite, and forsterite.

A secondary test that could be used in industry was also performed to determine the fluorophlogopite content of the fired mica. The mica solubility test is a method to dissolve fluorophlogopite from aa 0.500 g mica sample in boiling concentrated H_2SO_4 (10.0 N) while leaving behind insoluble secondary phases. The dry sample is weighed both before and after the solubility test, with the resulting weight difference being used to calculate the weight percentage of fluorophlogopite in the final product.

Another relatively simple procedure developed is the Fluoride Ion Selectivity Test. A 0.500 g sample of fluorophlogopite from the final product is mixed with 4.00 g $LiBO_2$, and fused at 900°C for 30 min, stirring the sample after 15 minutes to ensure complete fusion. The resulting material was then dissolved in a 0.5 N HCl acid solution and neutralized with 0.5 N NH_4OH. An Orion 90-09 Fluoride Ion Selective Electrode, connected to a Fisher millivolt meter, is then used to detect the presence of F^-, with the concentration of F^- calculated from the electric potential of the solution. From the detected F^- concentration, the amount of fluorophlogpite in the final product can then be calculated.

3.4 Particle Size Analysis

Particle size analysis was done using two procedures: Fisher Sub-Sieve Sizer (FSSS) test, an in-house quality check used in industry, and the Shimadzu Particle Size Analyzer (PSA) Model # SA-CP3, performed in the laboratory at Virginia Tech. The average particle size and particle size distribution of each sample were determined using both methods to see if any correlation exists between the two methods. Also, the particle size analysis was used to determine the milling time necessary to grind the final mica product to a desired particle size.

Four batches were milled separately in a single Paul O. Abbe Type B, No.6 All Steel Dry Pebble Mill. Before milling each batch, any remaining powder within the mill was removed by running a dry open mill for one hour. During testing, conditions were kept constant by running each batch at a speed of 31.6 rpm and using 688 lb of flint pebbles per load. Coarsely ground mica batches weighing 167 lbs (1/3 of a production-scale heat) were placed in the mill with 200 g samples being removed after the following total milling times: 5 and 30 minutes, 1, 2, 4, 8, 16, 24, and 32 hours. Each sample was then tested using the FSSS method and the Shimadzu PSA.

The FSSS test was conducted by three process operators to determine if the procedure was consistent and the results reproducible. A dry powder sample of fluorophlogopite was weighed out to the nearest 0.01 gram equal in weight to the theoretical density of the material (2.88 g/cm^3). The FSSS test was then performed

by specifically following the equipment manufacturer's instructions, with each operator recording the determined particle size.

The Shimadzu PSA, Model # SA-CP3 is a programmable particle size analyzer with variable settings, including operational mode (such as centrifugal, gravitation, and multi-mode) and disk acceleration rates. For the testing of the particle size distribution of fluorophlogopite, the Shimadzu PSA was set in the centrifugal operational mode, using a rate of acceleration of 240 rpm. This arrangement of settings was suggested by the manufacturer for the accurate determination of the distribution of particles having sizes of less than 20 μm. The Shimadzu PSA was programmed to divide the size distribution of the particles into three size categories: determining the size at which 14% of the particles were larger than the size indicated, the mean particle size of the sample (50%), and the size at which 86% of the particles were larger than the size indicated.

In performing the Shimadzu PSA, each dry powder sample was dispersed in an aqueous solution containing 0.050 wt% sodium pyrophosphate. A 0.10 g sample of fluorophlogopite was dispersed in 25 mL of this solution and using an ultrasonic probe in the sample for 3 minutes to get a uniform suspension. After ultrasonication, 10 drops of the suspension were pipetted into a clean quartz cell, as supplied by Shimadzu, filled to a predefined volume with a sodium pyrophosphate solution having the same concentration as the sonicated suspension. The resulting suspension is slightly translucent. After placing the lid on the quartz cell, the cell was rotated gently 2 to 3 times to homogeneously disperse the

fluorophlogopite suspension. The cell was then placed into the programmed Shimadzu PSA, locked into the disk-centrifuge system, and aligned with the light source. Finally, the programmed Shimadzu PSA cycle was then run.

4. Results and Discussion

4.1 Raw Material Composition and Blending

In processing fluorophlogopite, the role of the fluoride ion, F^-, is most important. K_2SiF_6 is by far the most volatile compound at reaction temperatures. Because of this inherent volatility, the F^- ion can readily escape from the batch. This loss of fluorine from the batch results in a decrease in the amount of fluorophlogopite produced during a solid-state reaction, and an increase is possible in the formation of fluorine-deficient phases such as spinel ($MgAl_2O_4$), forsterite (Mg_2SiO_4), and leucite ($KAlSi_2O_6$). Therefore, the first set of experiments was designed to evaluate the importance of the role of F^- in forming fluorophlogopite.

Initial XRD analysis patterns of production-scale heats consistently indicate the presence of two predominant phases: fluorophlogopite and spinel. To effectively determine the quantities of these phases present in a sample, reference samples were made from pure batches of these two predominant phases. These pure phases were processed from bench-scale procedures using the same raw materials used in

the fluorophlogopite production process. Reference patterns were then established using fluorophlogopite-spinel blends, from 55:45 to 95:5 wt% ratios (Appendix A). These reference patterns were then used to compare samples from various heats, both production and bench-scale, during this study. XRD analysis was used to determine phase percentages from both bench-scale and production-scale heats. All percentages, unless otherwise noted, are given in terms of weight percent.

Bench-scale experiments were done on batches having stoichiometric composition to determine the effect covering the samples has on fluorophlogopite formation. These batches were heated under similar conditions, with one batch in covered alumina containers and a similarly prepared batch in uncovered containers. A comparison of XRD patterns indicates that the samples from the covered batches had a significantly higher fluorophlogopite content than those from uncovered batches.

Tests were also conducted to determine the effect of fluorine content on the amount of fluorophlogopite formed during firing. XRD analysis confirmed that under similar firing conditions fluorophlogopite content increases with the amount of fluorine in the raw material blend.

In repeating these experiments under production heat conditions, various heats contained covered and uncovered cordierite saggers containing unpressed cakes of raw material blend. Batch compositions contained either stoichiometric amounts of raw materials or stoichiometric amounts with an additional 10% excess K_2SiF_6. The results of the bench-scale experiments were confirmed when the

batches containing 10% excess K_2SiF_6 yielded higher fluorophlogopite contents than batches with only stoichiometric compositions.

4.2 Material Compaction and Pressing

The effects of pressing the raw material blend on the formation of fluorophlogopite was then studied. During bench-scale experiments, it was discovered that pressing small raw material blend samples (2.00 g) into pellets using a pressure of 5000 psi, as recommended by Theodore and Beaver,[12] yielded higher fluorophlogopite percentages than unpressed samples. (It must be noted that both the pressed and unpressed samples were fired in covered alumina containers.) Examination of the samples seems to indicate that pressed samples have a lower loss of fluorine from the batch than unpressed samples. Also, a volume increase of up to 35% was observed in the fired pellets.

In studying the effects of pressing the raw material blend on production-scale firings, 13-lb. cakes pressed at 5000 psi were compared to unpressed cakes with the same weight of raw material blend. In both cases, all saggers on the cart were stacked so that each sagger was covered to minimize loss of free fluorine (Figure 4).

Experimental production-scale heats were then conducted to determine the composition of the final product based on these effects: firing temperature, product residence time (defined as the time the batch is in the furnace, including the heat-up, firing, and cool-down periods), amount of fluorine within the raw material blend,

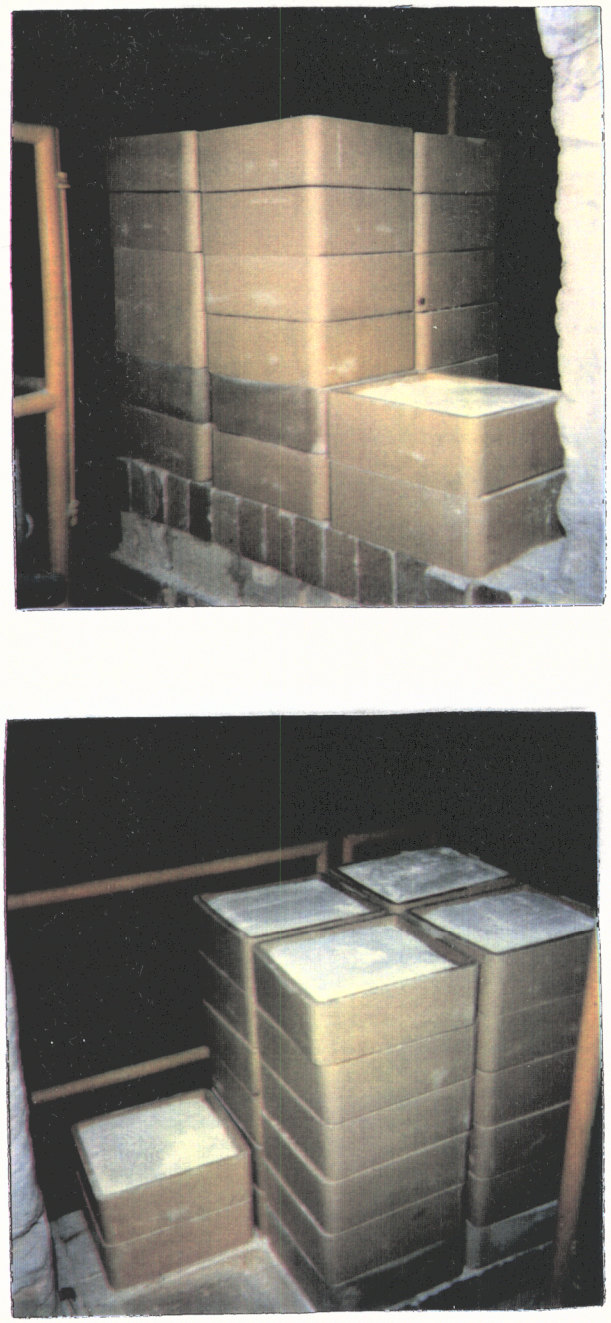


Figure 4. Stacking sequence of cordierite saggers used to minimize fluorine loss.

and pressing of the raw material blend. Tables 3 and 4 show a comparison of phase compositions for stoichiometric heats fired in a commercial furnace at or above the minimum established temperature of 1000°C for both 7 and 10 hours according to the central control thermocouple. The 10-hour heats had a higher fluorophlogopite content, and heats containing 10% excess F- had even higher amounts of fluorophlogopite than stoichiometric heats using the same firing times.

The key observation was that there was no difference in fluorophlogopite content between pressed and unpressed cakes, contradicting the results obtained from bench-scale experiments. This can be explained by the relative amount of the samples within their respective environments. The fluorophlogopite cakes processed from production-scale heats were tightly packed within the saggers, limiting the open space between the newly-formed cake and the sagger. Also, the volume of the saggers and fluorophlogopite present nearly filled the furnace to capacity. On the other hand, bench-scale experiments were carried out using small fluorophlogopite samples in a largely empty high-temperature furnace. It is believed that because of the small amount of open space within both each sagger and the entire furnace, the amount of free fluorine within the heat is more concentrated for production-scale runs than for bench-scale heats. This increase in fluorine concentration results in an increase in fluorophlogopite formation within a heat.

4.3 Mica Firing

An important factor in commercial batch-processing of fluorophlogopite is

Table 3. Comparison of phase composition of heats fired in production-scale furnace at or above 1000°C for 7 and 10 hours -- stoichiometric composition vs. 10% excess K_2SiF_6.

Batch Composition	7 hr. Mica	7 hr. Spinel	10 hr. Mica	10 hr. Spinel
Stoichiometric	66.5	33.5	74.4	25.6
10% excess K_2SiF_6	71.9	28.1	75.8	24.2

Table 4. Comparison of phase composition of heats fired in production-scale furnace at or above 1000°C for 7 and 10 hours -- pressed vs. unpressed cakes.

Cake Compaction	7 hr. Mica	7 hr. Spinel	10 hr. Mica	10 hr. Spinel
Pressed	69.6	30.4	75.6	24.4
Unpressed	68.5	31.5	75.0	25.0

reproducing firing conditions, including heating and cooling rates and the overall product residency time. Controlling these factors tends to minimize variations of the phases formed in the final product. To help establish this, bench-scale experiments were conducted to determine which set of conditions would consistently produce the desired final product. In order to closely follow the firing conditions within a production-scale furnace, all bench-scale experiments were conducted to have similar heating and cooling rates as the production-scale heats. The standardized heating rate is 200°C/hour, while the cooling rate was established at 100°C/hour.

Bench-scale experiments were conducted for various firing times and temperatures, and three raw material compositions were tested (stoichiometric, 10% and 20% excess K_2SiF_6). Table 5 shows that stoichiometric samples fired between 5 and 13 hours at 1100°C contain the highest fluorophlogopite content, while fluorophlogopite content did not appreciably change for firings up to 20 hours for compositions containing excess fluoride. However, small amounts of forsterite were detected along with the characteristic fluorophlogopite and spinel during the 20 hour firings. Also, Table 6 shows that for stoichiometric compositions processed using similar firing temperatures, not only do higher fluorophlogopite contents result for 13 hours than for 15 hours, but the formation of the secondary phases leucite and forsterite does not exist for temperatures below 1100°C for stoichiometric compositions fired for 15 hours or less. Similarly, samples containing 10% excess fluoride contained only fluorophlogopite and spinel when fired for 13 hours at temperatures below 1200°C.

Table 5. Mica samples produced from bench-scale experiments at constant temperature (1100°C)

Sample No.	Batch Raw Materials	Firing Time(h)	Mica sample composition (wt %) Mica	Spinel	Forsterite
MS-1932-05	Mica[1,2,3]	5	70	30	---
MS-1932-07	Mica[1,2,3]	7	70	30	---
MS-1932-10	Mica[1,2,3]	10	70	30	---
MS-1932-13	Mica[1,2,3]	13	70	30	---
MS-1932-15	Mica[1,2,3]	15	60	40	---
MS-1932-20	Mica[1,2,3]	20	55	35	10
M10-1932-05	Mica + 10% xs K_2SiF_6[2,3]	5	75	25	---
M10-1932-07	Mica + 10% xs K_2SiF_6[2,3]	7	75	25	---
M10-1932-10	Mica + 10% xs K_2SiF_6[2,3]	10	70	30	---
M10-1932-13	Mica + 10% xs K_2SiF_6[2,3]	13	80	20	---
M10-1932-20	Mica + 10% xs K_2SiF_6[2,3]	20	70	30	---
M20-1932-05	Mica + 20% xs K_2SiF_6[2,3]	5	85	15	---
M20-1932-07	Mica + 20% xs K_2SiF_6[2,3]	7	75	25	---
M20-1932-10	Mica + 20% xs K_2SiF_6[2,3]	10	70	30	---
M20-1932-20	Mica + 20% xs K_2SiF_6[2,3]	20	85	15	Trace

[1] Stoichiometric composition
[2] Covered samples
[3] Pressed pellets, 5000 psi

Table 6. Mica samples produced from bench-scale experiments for various firing times and temperatures

Sample No.	Composition	Heat Treatment °C/hr	(Weight %) Mica	Spinel	Leucite	Forsterite
MS-1502-1	Mica[1,2,3]	1050/15	60	40	---	---
MS-1503-1	Mica[1,2,3]	1100/15	55	45	Trace	Trace
MS-1504-1	Mica[1,2,3]	1150/15	45	45	10	Trace
MS-1505-1	Mica[1,2,3]	1200/15	30	40	30	Trace
MS-1506-1	Mica[1,2,3]	1250/15	25	35	40	Trace
MS-1301-1	Mica[1,2,3]	1000/13	70	30	---	---
MS-1302-1	Mica[1,2,3]	1050/13	70	30	---	---
MS-1303-1	Mica[1,2,3]	1100/13	40	40	20	Trace
MS-1305-1	Mica[1,2,3]	1150/13	20	30	40	10
MS-1306-1	Mica[1,2,3]	1200/13	10	20	55	15
MX-1301-1	Mica + 10% xs K_2SiF_6[2,3]	1000/13	85	15	---	---
MX-1302-1	Mica + 10% xs K_2SiF_6[2,3]	1050/13	80	20	---	---
MX-1303-1	Mica + 10% xs K_2SiF_6[2,3]	1100/13	85	15	---	---
MX-1305-1	Mica + 10% xs K_2SiF_6[2,3]	1150/13	95	5	---	---
MX-1306-1	Mica + 10% xs K_2SiF_6[2,3]	1200/13	75	20	Trace	Trace

[1] Stoichiometric composition
[2] Covered samples
[3] Pressed pellets, 5000 psi

Finally, Table 7 shows the phases that are present for stoichiometric raw material batches fired at various times and temperatures. For temperatures at or below 900°C the presence of unreacted raw materials is still apparent even after firing for 14 hours. The unreacted raw materials begin to disappear at 950°C but only after firing for a minimum of 10 hours, whereas no trace of raw materials exists after firing samples for at least four hours at 1000°C Note that at these low temperatures and times, spinel is the only secondary phase that is formed.

Another potential problem can happen if the raw material blend is fired too long or at too high a temperature, known as overfiring. When overfiring occurs, the free fluorine has a greater chance to escape from the saggers, again leading to the formation of secondary fluorine-deficient phases, primarily spinel. Table 6 shows that under bench-scale conditions, overfiring tends to decrease the amount of fluorophlogopite formed for samples of stoichiometric composition. The chance of overfiring at similar firing times and temperatures diminishes, however, for batches that contain excess fluorine.

The effects of overfiring can also be seen on the production-scale. Table 8 shows the differences in batch compositions for stoichiometric heats fired in the same furnace at the same temperature. Not only did the heat fired for 10 hours form a higher percentage of fluorophlogopite than the heat fired for 17 hours, but the spinel was the only secondary phase detected.

In the original set of procedures, 13 lb of the raw material blend were to have been pressed into cakes using a pressure of 5000 psi. These cakes were then

Table 7. Presence of phases at various firing times and temperatures.

	Firing time (hr.)	Phases present
	2	Raw material
	4	Raw material
	6	Raw material
850°C	8	Raw material, mica, spinel
	10	Raw material, mica, spinel
	12	Raw material, mica, spinel
	14	Raw material, mica, spinel
	2	Raw material
	4	Raw material, mica
	6	Raw material, mica
900°C	8	Raw material, mica, spinel
	10	Raw material, mica, spinel
	12	Raw material, mica, spinel
	14	Raw material, mica, spinel
	2	Raw material, mica
	4	Raw material, mica, spinel
	6	Raw material, mica, spinel
950°C	8	Raw material, mica, spinel
	10	Mica, spinel
	12	Mica, spinel
	14	Mica, spinel
	2	Raw material, mica, spinel
	4	Mica, spinel
	6	Mica, spinel
1000°C	8	Mica, spinel
	10	Mica, spinel
	12	Mica, spinel
	14	Mica, spinel

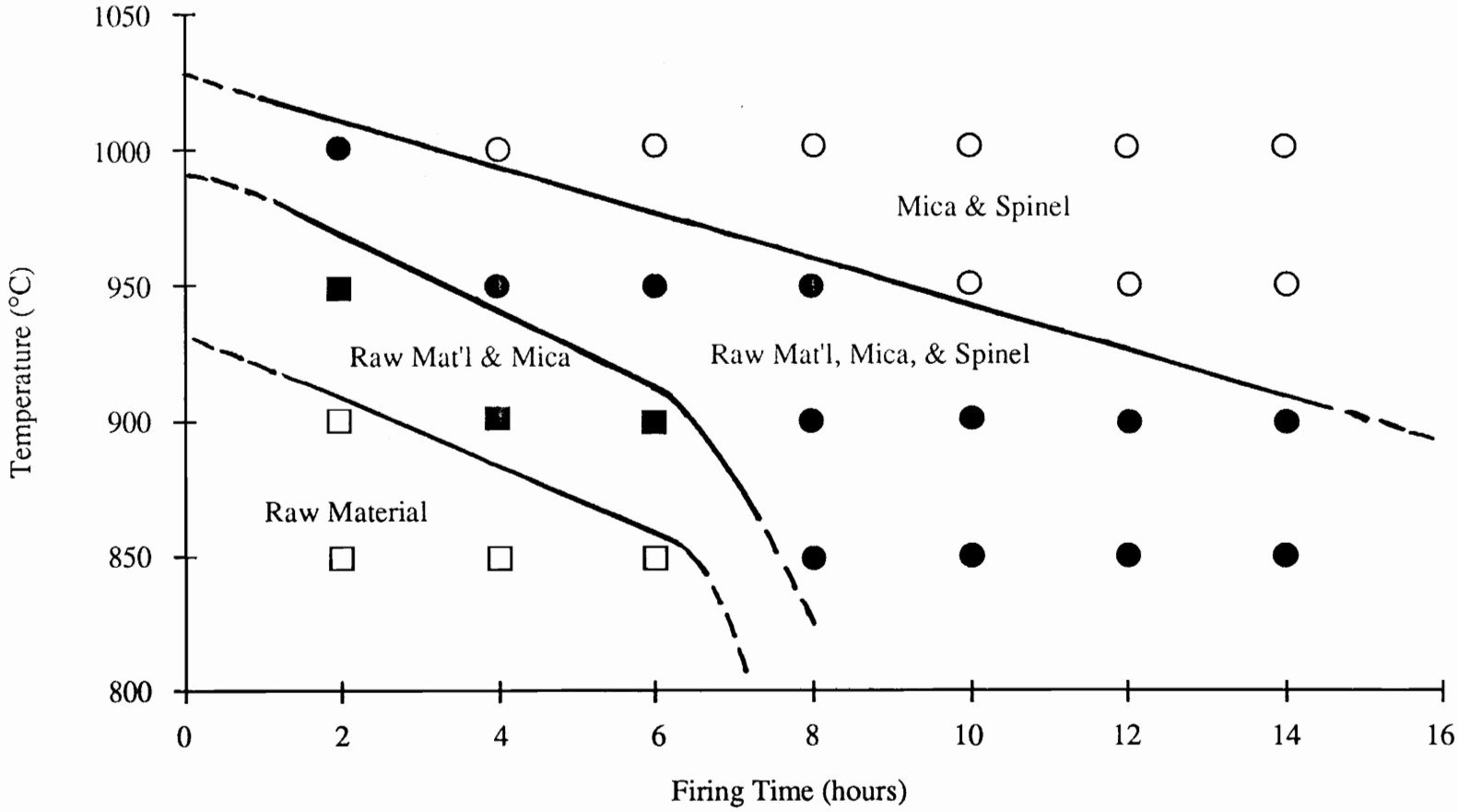


Figure 5. Preliminary Time-Temperature-Transformation diagram for fluorophlogopite formation

Table 8. Mineralogy of mica made with 10-hour heat cycle vs. standard 17-hour heat cycle (stoichiometric composition).

	(Weight %)					
	Mica		Spinel			
	Forsterite					
Cake Location	Normal*	H-803**	Normal	H-803	Normal	H-803
A - 1	80	75	20	25	Trace	--
A -12	70	75	30	25	--	--
A -13	75	85	20	15	5	--
B - 5	85	75	15	25	--	--
B - 8	70	80	20	20	10	--
B -13	80	80	20	20	Trace	--
C - 2	55	75	35	25	10	--
C -11	60	85	30	15	10	--
C -13	75	85	20	15	5	--
Mean	72.2	79.4	23.3	20.6	4.4	--
St. Dev.	9.7	4.6	6.6	4.6	4.6	--

*Normal - Furnace #2, 1200°C, 17 hours
**H-803 - Furnace #2, 1200°C, 10 hours

placed in cordierite saggers, and placed on the cart so that each sagger was covered, minimizing the escapes of free fluorine from the containers. The exposed saggers at the top of the cart were then covered with either cordierite sheets or with other saggers. The cakes were pressed to fit within the dimensions of the saggers. After firing, however, characteristic swelling of the cakes occurred to the point where some saggers became uncovered at some point during the heat. This opening of the saggers is undesirable because it permits the escape of free fluorine from the sagger, thereby decreasing the ability to form fluorophlogopite. It was also noted that the expansion was more pronounced along the height of the cakes rather than around the width, leaving open an unused volume of the saggers.

It should be noted that because the process is indeed a batch process used for producing a large quantity of fluorophlogopite (up to 500 lb per heat), the heating conditions and the thermal gradients within the production-scale furnaces are not as uniform as those used in the lab. Factors such as air flow within the furnace, insufficient control of the Globar heating rates, the amount of material within the furnace and bulk thermal conductivity of both the batch and containers can produce inconsistent thermal gradients within the furnace. Because of this, the results obtained from bench-scale experiments cannot be scaled-up directly to production-scale.

To help minimize this problem, four Type K (chromel/alumel) thermocouples were placed within the commercial furnace to determine the actual thermal gradient within the furnace, as shown in Figure 6. Previously, the firing times and

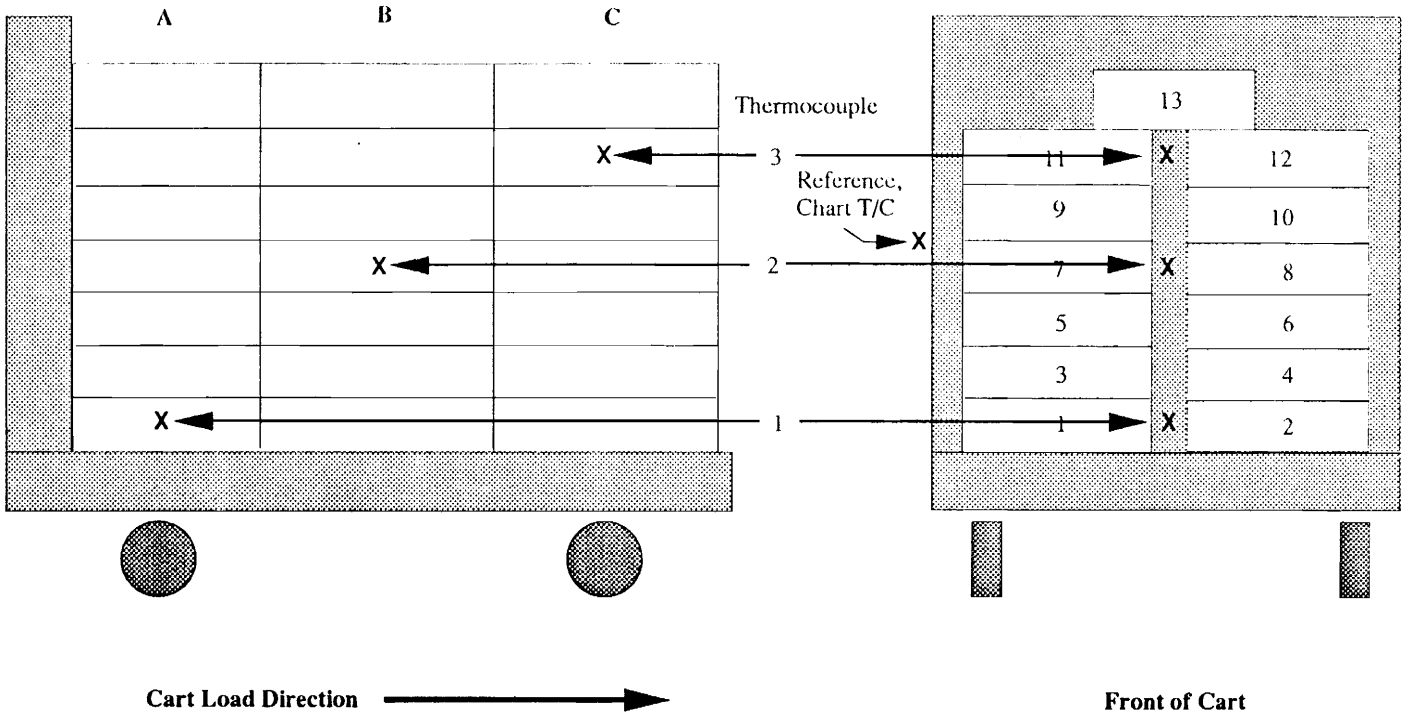


Figure 6. Standard thermocouple placements used in determining thermal gradients in production furnace.

temperatures of production runs were done using the readings indicated by a control thermocouple placed at the side of the furnace, directly next to the Globars (indicated as Reference Thermocouple). Figure 7 shows an example of a typical thermal gradient of a commercial heat. As expected, the heating rate next to the control thermocouple located adjacent to the Globars was much higher than heating rates indicated by thermocouples placed in the middle of the heat. Examination of Figure 7 shows the two Control Thermocouples indicate a firing temperature of 1200°C was reached within five to seven hours, while the thermocouples in the middle of the heat had only reached 815°C. Also, the temperature of the middle of the heat routinely did not reach the expected firing temperature of 1200°C, indicating underfiring of the heat was apparent and, therefore, limiting the formation of fluorophlogopite.

In order to standardize heating procedures, a central monitoring thermocouple was recommended to establish a standardized minimum firing time and temperature within a given heat. This would avoid the problem of indicating artificially high temperatures of the overall heat.

4.4 Milling and Particle Size Analysis

The FSSS and Shimadzu PSA methods were compared to determine the mean particle size and distribution of four sample batches at pre-determined milling times. Close examination of the data in Table 9 shows that the particle sizes determined from the FSSS were generally smaller for batches milled for the same

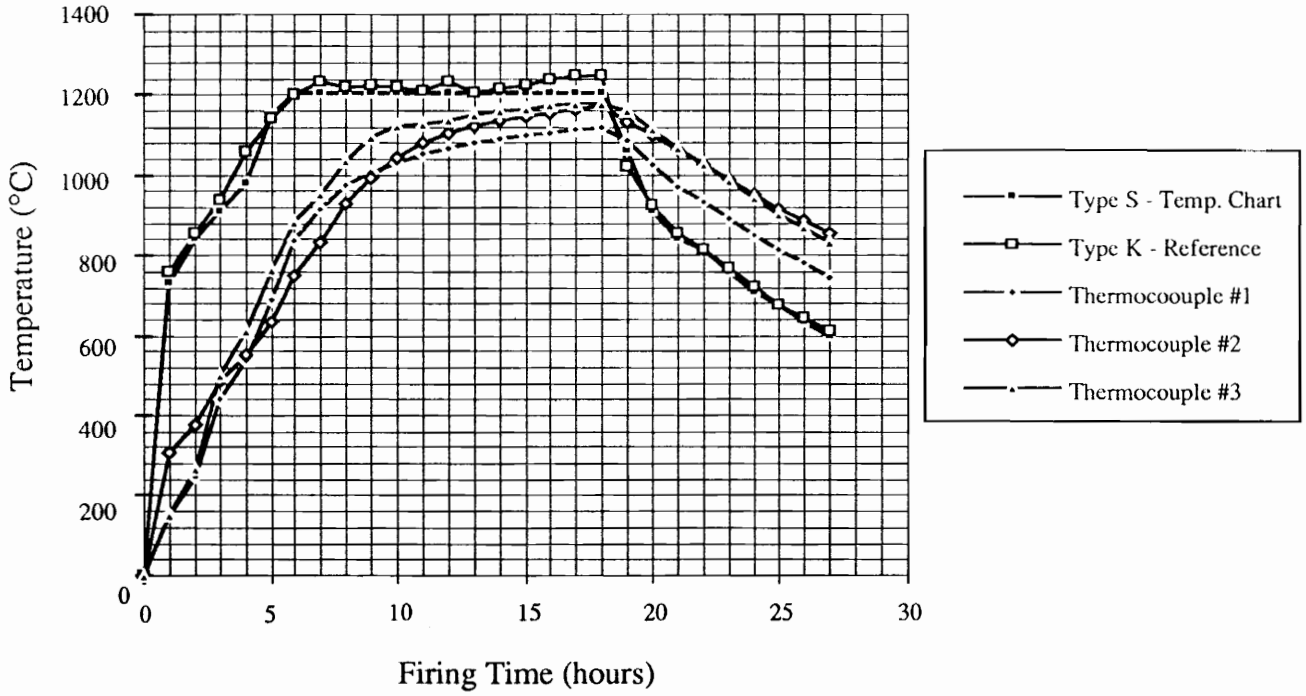


Figure 7. Representative thermal gradients in commercial furnace for heat held for 10 hours at or above 1000°C according to reference thermocouple.

Table 9. Particle size analysis using the Fisher Sub-Sieve Sizer and the Shimadzu Particle Size Analysis (particle sizes in microns).

		FSSS Test*			Shimadzu		
	Milling time	#1	#2	#3	14 %	50 %	86 %
	5 min.	3.10	5.25	5.10	7.40	5.35	1.29
	30 min.	2.20	3.80	3.70	7.01	4.67	1.86
	1 hr.	1.70	3.20	3.30	7.01	4.72	1.92
	2 hrs.	1.20	3.20	2.50	6.63	3.89	1.47
HEAT H-851-1	6 hrs.	2.40	2.20	2.10	6.75	3.33	0.93
	8 hrs.	1.45	1.50	1.75	5.21	2.22	0.76
	16 hrs.	1.20	1.40	1.55	5.19	1.76	0.69
	24 hrs.	1.45	1.45	1.50	5.36	2.04	0.77
	32 hrs.	1.40	1.50	1.50	4.77	1.76	0.69
	5 min.	5.60	5.45	5.30	7.32	5.06	1.26
	30 min.	3.35	3.60	3.70	7.03	4.51	1.17
	1 hr.	3.00	3.05	2.95	6.94	4.04	0.96
	2 hrs.	2.20	2.40	2.55	6.66	3.20	0.79
HEAT H-851-2	4 hrs.	2.00	1.80	2.20	6.89	3.15	0.78
	8 hrs.	1.20	1.50	1.90	5.98	2.65	0.88
	16 hrs.	1.50	1.55	1.55	4.69	2.20	0.78
	24 hrs.	1.00	1.00	1.60	3.36	1.30	0.63
	32 hrs.	1.45	1.45	1.60	1.99	1.06	0.49
	5 min.	6.40	6.45	4.20	7.31	4.63	1.30
	30 min.	3.70	3.50	2.85	6.95	4.23	2.01
	1 hr.	2.90	3.10	2.85	5.82	3.38	1.12
	2 hrs.	2.50	2.45	2.35	6.71	2.87	0.77
HEAT H-851-3	4 hrs.	2.10	2.15	2.00	5.99	2.28	0.69
	8 hrs.	1.50	1.50	1.90	5.13	1.97	0.70
	16 hrs.	1.78	1.71	1.80	4.41	1.65	0.61
	24 hrs.	1.50	1.45	1.75	3.79	1.44	0.60
	32 hrs.	1.20	1.00	1.60	3.43	1.33	0.61
	5 min.	4.40	4.60	3.80	7.38	5.09	1.35
	30 min.	3.40	3.20	2.80	6.98	4.68	1.35
	1 hr.	2.60	2.40	2.30	7.09	4.39	0.80
	2 hrs.	2.60	2.50	2.15	6.26	2.93	0.70
HEAT H-853-1	4 hrs.	1.95	1.90	1.90	6.39	2.30	0.70
	8 hrs.	1.70	1.70	1.70	6.70	2.13	0.65
	16 hrs.	1.60	1.50	1.55	4.99	1.80	0.70
	24 hrs.	1.45	1.40	1.40	4.40	1.52	0.58
	32 hrs.	1.40	-----	1.35	2.29	1.15	0.56

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* - Testing performed by three process operators

amount of time than results obtained from the Shimadzu PSA. According to the manufacturer's procedures, the fluorophlogopite was originally milled for 30 minutes to get a mean particle size of 3.7 μm, whereas 2 hours were needed for a mean particle size of 2.2 μm. To obtain a mean particle size of 3.7 μm, the FSSS method indicates 30 minutes milling time is necessary. However, Shimadzu PSA results show at least 2 hours is needed. Table 9 also shows that FSSS indicates four hours of milling time were needed to obtain fluorophlogopite particles with a minimum median size of 2.2 μm, while Shimadzu PSA tests indicate a minimum of eight hours was needed to reduce the fluorophlogopite to the same size.

There are advantages and disadvantages for each of these two methods. While the FSSS indicates only the mean particle size of a batch, the Shimadzu PSA can also provide the particle size distribution, as shown in Table 9. Secondly, inconsistent measurements occur frequently when using the FSSS method, indicating this test is operator dependent. However, the FSSS test is a relatively simple procedure, requiring only a dry powder sample for testing, and can be used in industry by process operators. The Shimadzu PSA is considerably more difficult to use in an plant environment, generally requiring extensive training by laboratory technicians to get dependable results. Although the FSSS should not be used to determine the actual mean particle size, it can be used as a guide to the milling times required to obtain a desired particle size.

4.5 Material Testing Procedures

Table 10 shows the results of the mica solubility test, where the percentage weight loss indicates the phlogopite content of a fired sample. There are advantages and disadvantages to this procedure. The advantages are that it effectively removes fluorophlogopite from the final product, and that it is a relatively simple procedure. However, the high acid concentration necessary (> 10.0 N) to effectively dissolve the fluorophlogopite poses safety concerns for the laboratory technicians. Also, at least four hours are needed to test each sample, and working with a small sample size (0.50 g fluorophlogopite/500 mL solution) required for best results can be subject to human error.

The Fluorine Ion Selectivity Test, on the other hand, consistently and accurately determines the amount of fluorophlogopite produced in the final mica product. The advantages of this procedure are that if done accurately, the amount of fluorophlogopite in the material can accurately be determined. And although sample preparations may be time consuming (up to two hours), many samples can be prepared simultaneously; testing time per sample is approximately 20 minutes. Final results are not presented here because this method is still being tested in industry.

Table 10. Solubility of mica samples dissolved in various concentrations of sulfuric acid (H_2SO_4) solutions.

		Weight of mica sample (g)		
Concentration	Temp. (°C)	before test	after test	% wt loss*
18.0 M	100°C	10.00	6.26	37.4
18.0 M	100°C	6.00	2.20	63.3
18.0 M	100°C	4.01	1.32	67.1
18.0 M	100°C	1.99	0.58	70.8
10.0 M	100°C	10.01	6.02	39.9
10.0 M	100°C	6.02	2.35	61.0
10.0 M	100°C	3.99	1.26	68.4
10.0 M	100°C	2.00	0.68	66.0
5.0 M	100°C	10.00	6.53	34.7
5.0 M	100°C	6.01	2.40	60.0
5.0 M	100°C	4.00	1.44	64.0
5.0 M	100°C	2.01	0.64	68.2

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* - phlogopite content (wt%) in final product

5. Conclusions

The following results have been found from bench-scale and production-scale experiments:

1. The addition of excess K_2SiF_6 was found to increase the amount of fluorophlogopite while simultaneously decreasing the presence of fluorine-deficient phases, such as leucite and forsterite.

2. Placing the raw material blend within closed containers is necessary to limit the loss of fluorine into the atmosphere from the batch.

3. The minimum firing temperature necessary to ensure complete reaction of the raw materials was found to be 1000°C.

4. The formation of secondary fluorine-deficient phases, primarily forsterite and leucite, appears to occur due to batch overfiring.

5. For production-scale solid-state batch processing of fluorophlogopite, pressing of the raw materials into cakes appears to have no effect on the formation of fluorophlogopite.

6. The Fluoride ion selectivity test can accurately determine the amount of fluorophlogopite in a given sample provided that it is the only fluoride present in that sample.

7. No direct correlation can be made between the Fisher Sub-Sieve Sizer test and the Shimadzu Particle Size Analysis.

From these results, the following recommendations have been made:

1. 10% excess K_2SiF_6 should be added to a raw material blend to increase the fluorophlogopite content of a fired batch and to limit the formation of undesirable secondary phases.

2. To reduce processing time, the pressing step of the raw material blend should be eliminated. Instead, 13 lb of the powdered blend should be placed in closed cordierite saggers.

3. To standardize the firing temperature and time, a central control thermocopule should be used to properly monitor the minimum firing temperature within the furnace.

4. The firing temperature should be lowered from 1200°C to 1000°C, while the firing time should be decreased from 17 to 10 hours.

This information will be used by the sponsor in future planning, including the possibility of process expansion. Initially, the sponsor planned to double the capacity of the material produced by doubling the size of the process. However, since this project resulted in increasing material output while decreasing overall processing time by 30%, long term capital investments were deemed unneccessary and were not made.

Results of this project can also be expanded upon in the future. One possible project includes the use of fluorophlogopite in polymer-composites for structural and electrical applications.

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7. Appendix A

Determination of Fluorophlogopite Content in Processed Samples Using X-ray Diffraction Patterns

Since it was established that the two predominant phases produced from this solid-state batch mica process were fluorophlogopite ($KMg_3AlSi_3O_{10}F_2$) and spinel ($MgAl_2O_4$) standard X-ray diffraction patterns were made using each of these materials. The samples for these patterns were produced by blending the two components using the following fluorophlogopite-spinel compositions by weight: 95-5, 85-15, 75-25, 65-35, and 55-45. These standards were then scanned using the procedures described earlier in Section 3.3.

Mica content of a sample is determined by comparing its diffraction pattern to the standard patterns shown in Figures A.1 - A.5. Figure A.1 shows that the fluorophlogopite peaks of a nearly pure fluorophlogopite sample (95-5) are sharp and distinct, especially when compared to the spinel peaks. Also, the number of fluorophlogopite peaks appearing in the 2 range of 20° to 50° far outnumber the spinel peaks, as expected. However, as the amount of spinel in the sample

increases and fluorophlogopite content decreases, the number and intensities of the spinel peaks also increase when compared to the fluorophlogopite peaks. For compositions below 75-25 (Figure A.3), it may be difficult to distinguish between fluorophlogopite and spinel peaks as shown by comparing Figure A.2 for 85-15 and Figure A.5 for 55-45.

As an example, Figure A.2 shows that the relative intensities of fluorophlogopite peaks are much higher than adjacent spinel peaks in two regions: 36°-38° and 44°-46°. However, the intensities of the spinel peaks increased with spinel composition in the standard while the intensities of the fluorophlogopite peaks decreased. Figure A.5 shows the results of increasing spinel content in the standard and the resulting increase in peak intensities. Not only does the spinel peak have a higher intensity than the fluorophlogopite peak in the 44°-46° region, but the spinel and fluorophlogopite peaks become indistinguishable in the 36°-38° region. The appearance of another spinel peak at 31.5° in the 55-45 standard pattern (Figure A.5) is another indicator of increased spinel content.

Standard X-ray diffraction patterns can be used effectively to determine the composition of the mica produced from this solid-state batch process. Comparing the intensities of neighboring fluorophlogopite and spinel peaks in the 20°-50° region and the appearance of new spinel peaks in patterns from samples containing higher amounts of spinel are the primary indicators of phase composition for the processed mica.

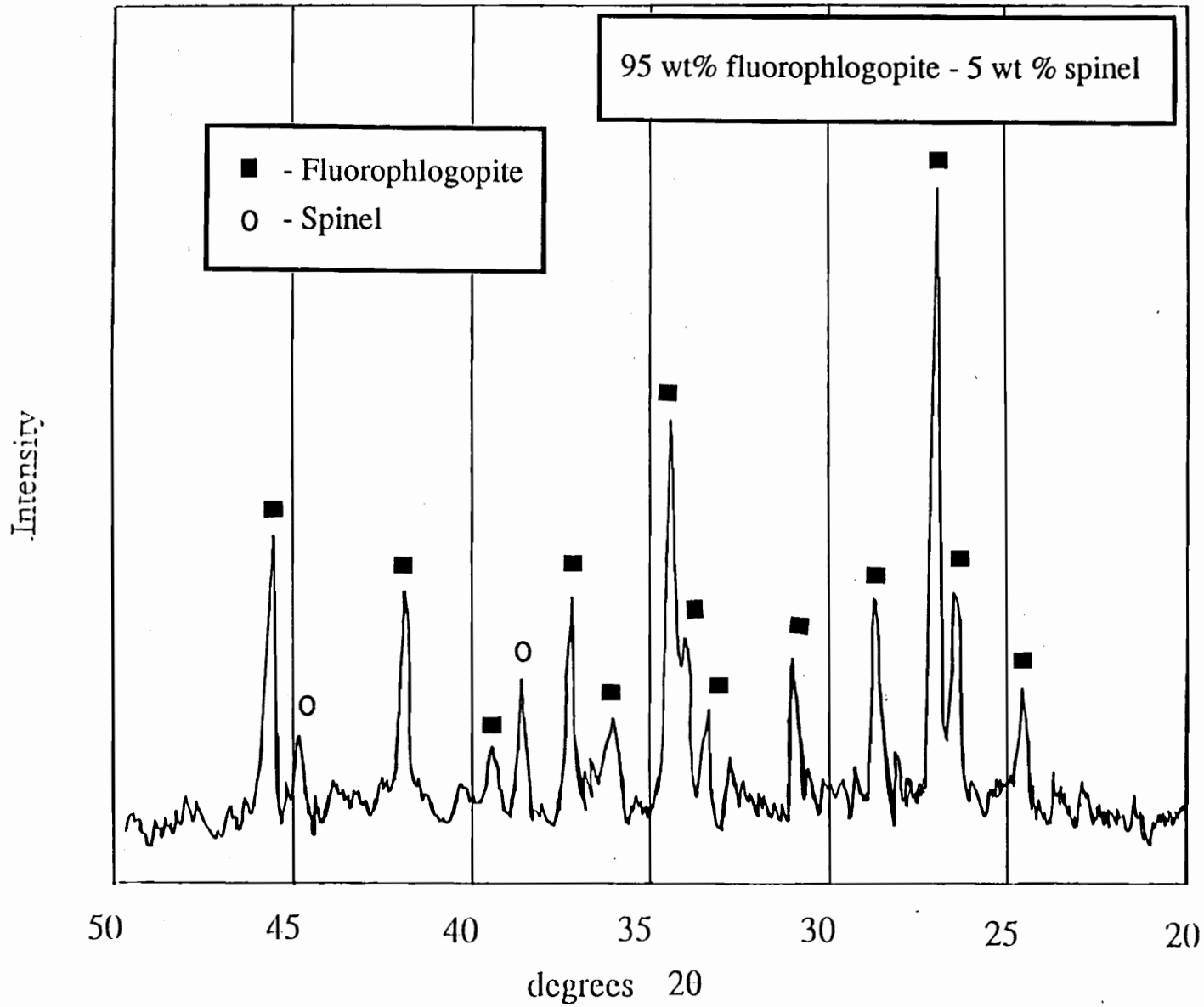

Figure A.1. Standard X-ray diffraction pattern for sample containing 95 wt% fluorophlogopite - 5 wt% spinel

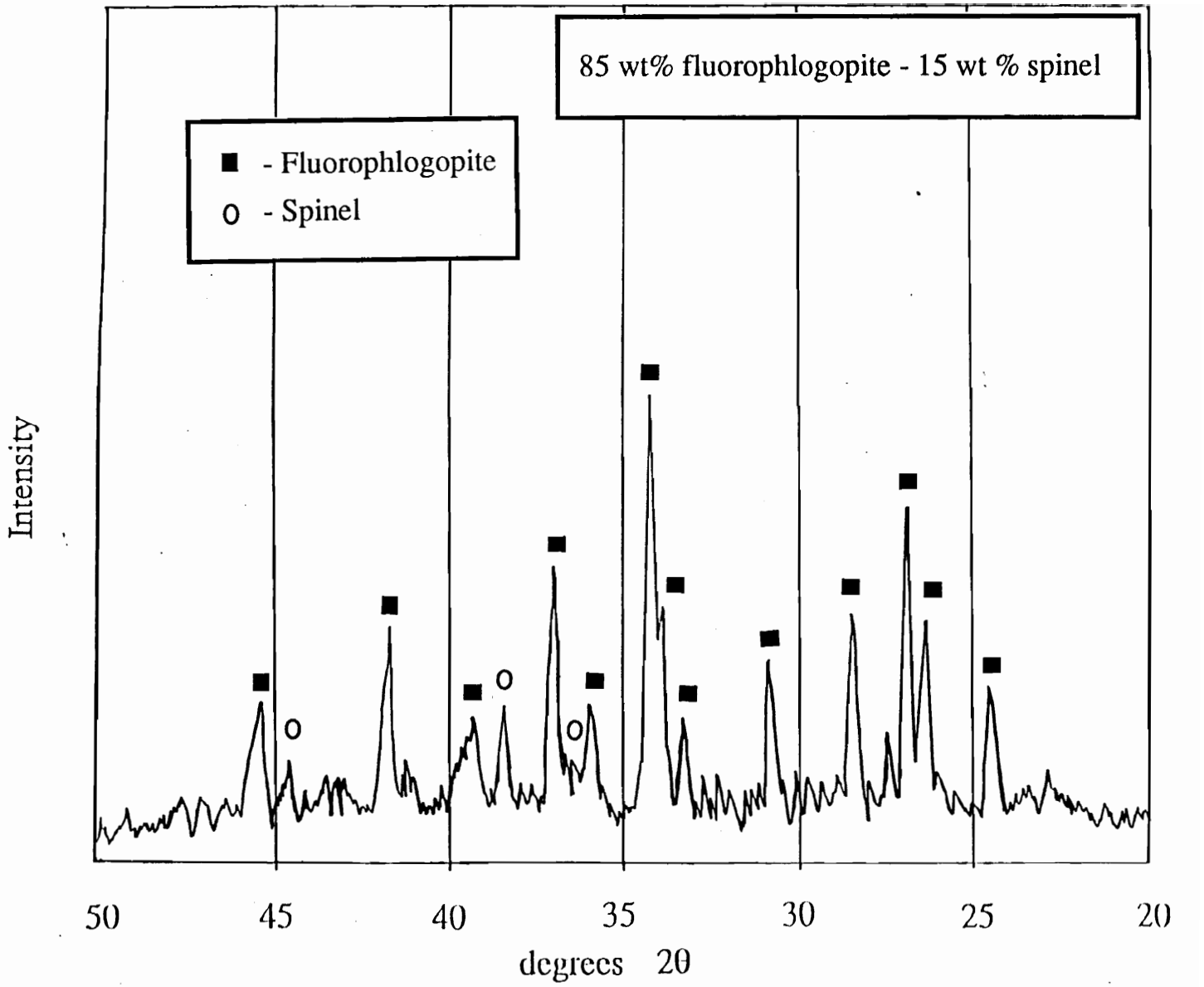

Figure A.2. Standard X-ray diffraction pattern for sample containing 85 wt% fluorophlogopite - 15 wt% spinel

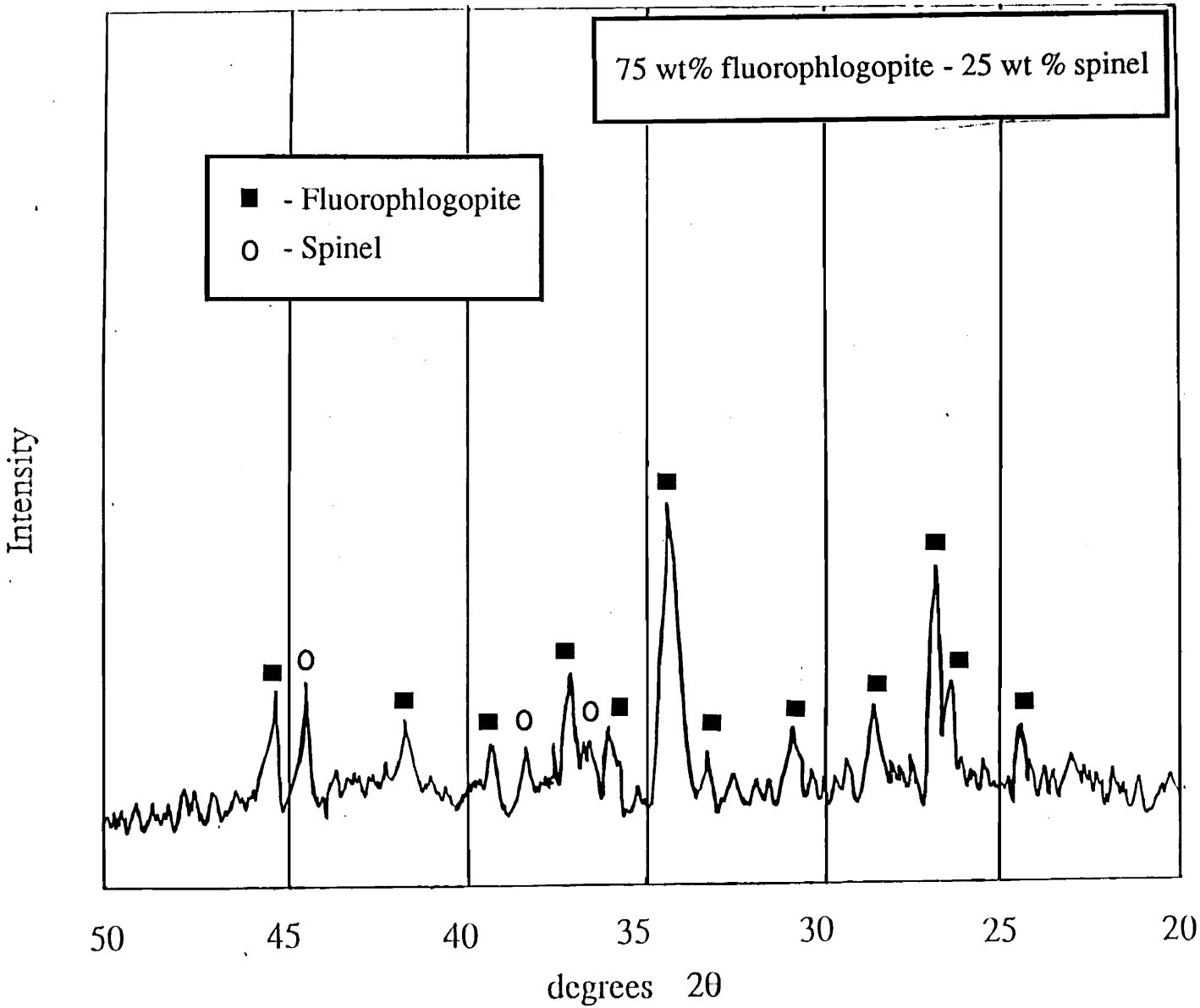

Figure A.3. Standard X-ray diffraction pattern for sample containing 75 wt% fluorophlogopite - 25 wt% spinel

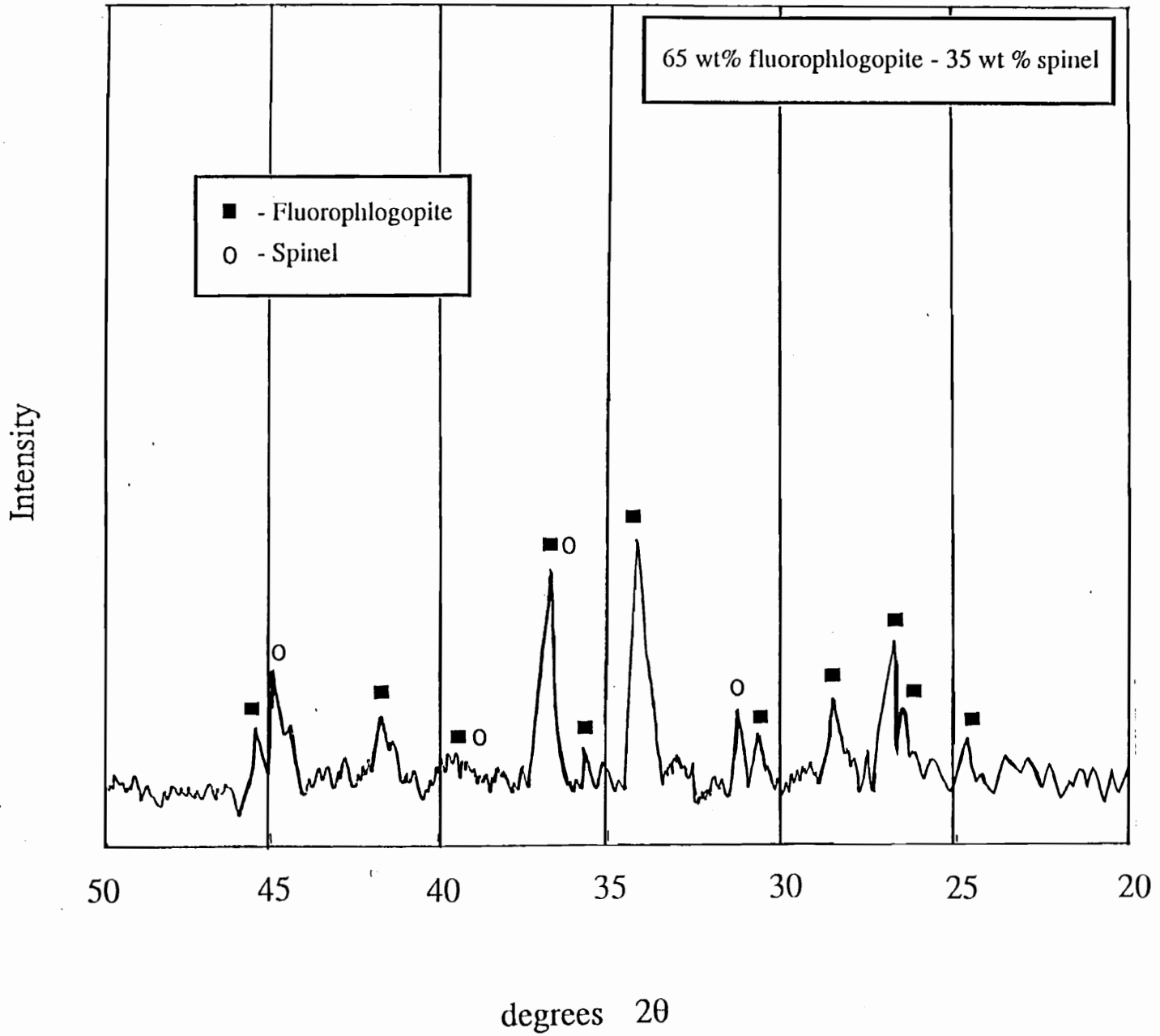

Figure A.4. Standard X-ray diffraction pattern for sample containing 65 wt% fluorophlogopite - 35 wt% spinel

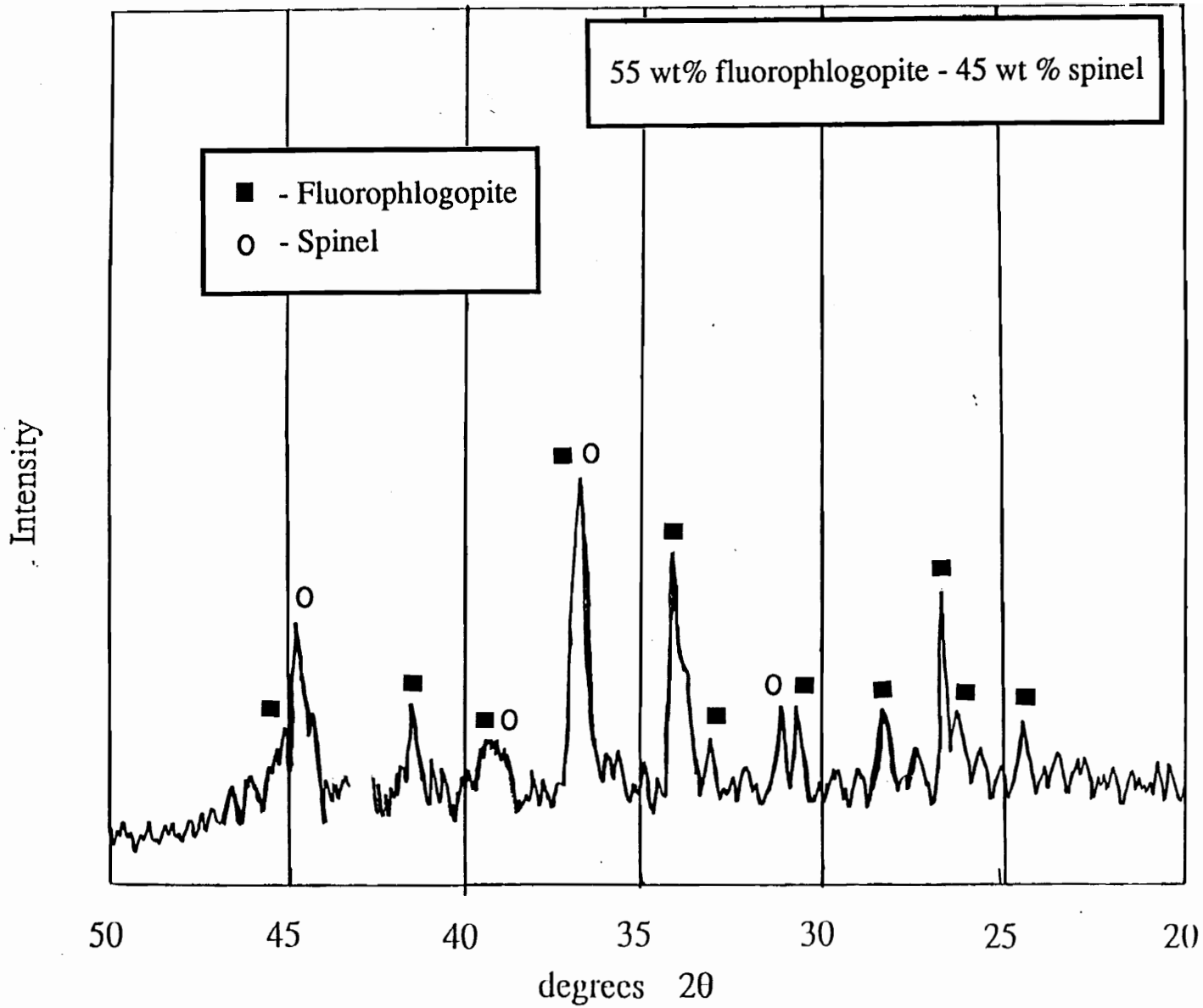

Figure A.5. Standard X-ray diffraction pattern for sample containing 55 wt% fluorophlogopite - 45 wt% spinel

8. Vita

Robert H. Howell, Jr. was born in Norfolk, Virginia, on February 19, 1967, the son of Robert H. and Martha P. Howell. He was graduated from Green Run High School in Virginia Beach, Virginia, in the Spring of 1985, whereupon he entered Virginia Polytechnic Institute and State University in the Fall of 1985. He then received his Bachelor of Science degree in Materials Engineering in May, 1990. As an undergraduate, Bob served as Secretary of the Virginia Tech student chapter of ASM during the 1988-1989 academic year, and as President of the Virginia Tech chapter of the American Ceramic Society in 1989-1990. He continued his education at Virginia Tech immediately after graduation by pursuing a graduate degree in Materials Science and Engineering, where he completed the requirements for his Master of Science degree in the Spring of 1992.