Articles

Novel Energy-Saving Materials for Microwave Heating

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Novel foams and plates of $Fe_2O_3-Li_2O-SiO_2-Al_2O_3$ composition made from a mixture of Fe_3O_4 and petalite mineral have been discovered to get rapidly heated under microwave irradiation and have relatively high heat energy holding ability compared to the presently used commercial ceramics. The Fe_3O_4 component transformed to Fe_2O_3 is responsible for microwave-assisted rapid self-heating of the composites and the relatively low thermal conductivity of these composites leads to their high heat holding ability. These novel ceramics are being commercialized as microwave ware. They also have potential applications in remediation of organic contaminants by facilitating ultrafast decomposition upon microwave irradiation as demonstrated with cooking oil as an example.

Introduction

The use of microwaves in solid-state sintering and the hydrothermal synthesis of ceramic materials[1–17] have been well-documented. Microwave-assisted synthesis and sintering are generally much faster, cleaner, and more economical than the conventional methods. Advantages such as rapid heating, selective material coupling, and enhanced reaction kinetics make the microwave process an attractive route for materials synthesis. A number of transition metal containing oxides such as Co_2O_3, CuO, Fe_3O_4, MnO_2, WO_3, NiO, V_2O_5, $CoFe_2O_4$, $ZnFe_2O_4$, $NiFe_2O_4$, NiO-$(Ce,Sm)O_2$, etc., are known to couple strongly to microwaves at ordinary temperatures,[2,4,5,10,12] and get heated up very rapidly. In these materials, the conductive or magnetic phases will absorb microwave energy far more rapidly due to dielectric and joule losses. Magnetic Fe_3O_4 is one of the most useful ferromagnetic oxides with a high value of tan δ_μ (magnetic equivalent of tan δ). The high tan δ_μ is probably responsible for triggering thermal runaway in these materials and therefore, it could be expected as the source material for rapid self-heating by microwave irradiation even though Fe_3O_4 is thermally not stable due to its transformation to γ and α-Fe_2O_3 over 200 °C ($4Fe_3O_4 + O_2 \rightarrow 6\ \gamma$- or α-Fe_2O_3). There are no previous reports on the effect of addition of Fe_3O_4 powder into low thermal expansion ceramics on the rapid self-heating, thermal properties, and the phase formation in these composites.

Here we report the discovery of a novel $Fe_2O_3-Li_2O-SiO_2-Al_2O_3$ composite, which has self-heating and heat retaining properties for applications as microwave ware such as plates (see the Supporting Information, Figure S1), rice cooker (see the Supporting Information, Figure S2), etc. The plates could be useful to keep food hot during delivery, for example and rice could be prepared more rapidly using containers made of these materials using microwave irradiation. Plates of novel $Fe_2O_3-Li_2O-SiO_2-Al_2O_3$ composition made from a mixture of Fe_3O_4 and petalite mineral have been discovered to get rapidly heated under microwave irradiation and have relatively high heat energy holding ability compared to the presently used commercial ceramics. The Fe_3O_4 component transformed to Fe_2O_3 is responsible for microwave-

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assisted rapid self-heating of the composites and the relatively low thermal conductivity of these composites leads to their high heat holding ability. These novel ceramics are being commercialized as microwave ware. The plates and porous foams also have potential applications in remediation of organic contaminants by facilitating ultrafast decomposition upon microwave irradiation as demonstrated with cooking oil as an example.

Experimental Section

Synthesis of Materials. Petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$, KCM Co., Japan) and magnetite (Fe_3O_4, 99%, Wako Pure Chemical Ind., Ltd., Japan) powders were used as the starting materials. The chemical composition of petalite is as follows: SiO_2:58.45, Al_2O_3:30.89, Na_2O:0.37, K_2O:0.45, CaO:0.30, MgO:0.28, Fe_2O_3:0.97, TiO_2:0.32, Li_2O:2.26, and loss of Ig is 5.98 wt %. Raw powders of 80 wt % petalite and 20 wt % magnetite were well-mixed using a ball mill with binder and water for 5 h, and the composition of Fe_3O_4 was changed from 0 to 20 wt %. Preparation of α-Fe_2O_3−Li_2O−SiO_2−Al_2O_3 composite foams is as follows: Polyurethane foam (diameter, 50 mm; height, 30 mm; cell number, 8 cell/25 mm; INOAC Co., Japan) was used as a substrate for making ceramic foam. Polyurethane foam was dipped into the slurry and pressed by two plates to remove residual slurry. To enhance the adhesion of ceramic powders onto polyurethane foam, we mixed 0.2 wt % lignosulfonic acid (sodium salt type, Sigma Ardlich, USA) with the slurry. After being dried at 40 °C, polyurethane foam coated with ceramic slurry was fired at 300 °C for 4 h and then at 500 °C for 1 h to burnoff organic substances, and finally sintered at 1100−1250 °C for 2 h. Plates of α-Fe_2O_3−Li_2O−SiO_2−Al_2O_3 composite were prepared as follows: The ball milled 20 wt % Fe_3O_4−petalite mineral powders were formed into plates ($50 \times 20 \times 7.5$ mm^3) by slip casting using a gypsum mold and sintered at 1100, 1150, 1200, and 1230 °C for 2 h. A modified domestic microwave oven (see the Supporting Information, Figure S3) with 2.45 GHz was used for microwave heating at different power levels and to different temperatures. The commercial domestic microwave oven (type, YD - 17W; magnetron power, 100 V to 1 KW; frequency, 2.45 GHz; output of power, multi-mode type; interval time of ON/OFF of output, 5 s; cavity size, $270 \times 280 \times 210^h$ mm^2; Yoshii Electric Co. Ltd., Japan,) was modified for self-heating tests of Fe_3O_4−petalite foam and plate composites as shown in Figure S3 of the Supporting Information. The modified oven was composed of the sample supporting quartz plate ($250 \times 250 \times 3^t$ mm^3) with 4 Teflon rods ($30^d \times 50^h$ mm^2) and turning fan with 6 rpm. The composite foam ($45^d \times 26^h$ mm^2) and plate ($46 \times 17 \times 6^t$ mm^3) sintered at 1200 °C were placed at the center of the quartz plate without any surrounding ceramic insulation. The surface temperature of the samples was continuously measured using fiberoptic thermometer (type, FL-2000; measurement temperature range, − 150 to 450 °C; Anritsu Meter Co. Ltd., Japan) during microwave irradiation. The sensor of fiberoptic thermometer was calibrated at 4 and 98 °C using a Hg thermometer without color calibration. The sensor tip was in direct contact with the surface of the samples. Temperature measurements in a microwave field are not an easy issue.[18] The system we used here gives relative measurements for comparison.

The sample microstructure and the crystalline phases were examined using a scanning electron microscope (FE-SEM; model 6700FS, JEOL, Japan) and powder X-ray diffraction (XRD) (model X'Pert-MRD, PANalytical Co., Japan) using Cu Kα radiation, respectively. In this investigation, we used two commercial wares for comparison. The commercial ware (1) has the following composition: 62.32:32.15:0.41:0.38:0.31:0.23:0.71:0.41:3.06 wt % SiO_2:Al_2O_3:Na_2O:K_2O:CaO:MgO:Fe_2O_3:TiO_2:Li_2O and commercial ware (2) has the following composition: 78.83:15.47:0.13:2.92:0.02:0.14:0.42:0.04 wt% SiO_2:Al_2O_3:Na_2O:K_2O:CaO:MgO:Fe_2O_3:TiO_2.

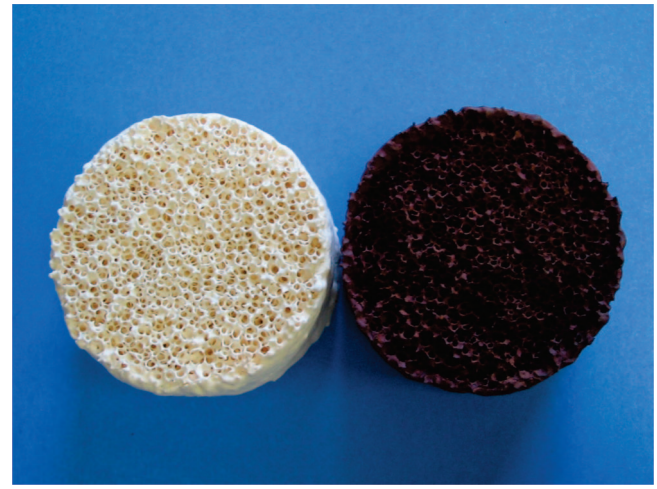

Figure 1. (a) Petalite foam and (b) 20 wt % Fe_3O_4−petalite foam sintered at 1200 °C for 2 h.

Thermal and Porous Properties of the Composites. The bulk densities of 20 wt % Fe_3O_4−petalite composite plates sintered at 1100−1230 °C were measured on the basis of Archimedes' method in water at 20 °C. Thermal properties such as specific heat, thermal diffusivity, and thermal conductivity of the composite plates were measured using a thermal constants measurement system (model FA-8510B, Rigaku Co., Japan). The thermal expansion coefficients of the composites up to 1200 °C were measured using a thermo-mechanical analyzer (model TMA 4020, MAC SCIENCE Co., Japan).

Decomposition of Oil. To investigate the application of the composite under microwave irradiation, we investigated the removal test of commercial cooking oil coated onto the 20 wt % Fe_3O_4−petalite composite plate. One gram of oil was coated onto the composite plate ($50 \times 20 \times 7.5$ mm^3), and was irradiated in the microwave oven with 600 W of power. The weight loss of oil was measured for 150 s at 26 to 830 °C.

Results and Discussion

Synthesis of Composite Foam. Figure 1 shows the morphologies of 17.0 g of petalite foam without Fe_3O_4 (Figure 1a) and 20 wt % Fe_3O_4−petalite composite foam (Figure 1b) sintered at 1200 °C, and their bulk densities were 0.37 and 0.39 g/cm^3, respectively. In the case of the composite foam, the sample was softened over 1250 °C because of increased formation of glassy phase and small bubbles in the composite. Figure 2 shows the XRD pattern of 20 wt %Fe_3O_4−petalite composite foam sintered at 1200 °C, and the sample was mainly composed of lithium aluminum silicate (Powder Diffraction File 53−1278, Li_2O Al_2O_3 $7.5SiO_2$, International Center for Diffraction Data, Newtown Square, PA) and α-Fe_2O_3. A small amount of mullite and alumina phase were detected. There were some small unidentified peaks at $2\theta = 27.8$, 34.4, 42.4, and 48.2°. However, Fe_3O_4 was not detected, as it is not a thermally

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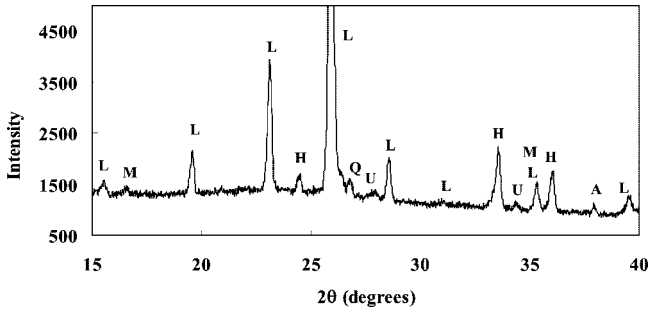

Figure 2. XRD patterns of 20 wt % Fe_3O_4−80 wt % petalite foam sintered at 1200 °C. L, lithium aluminum silicate; H, hematite(α-Fe_2O_3); M, mullite; Q, quartz; A, alumina; C, α-cristobalite; U, unknown.

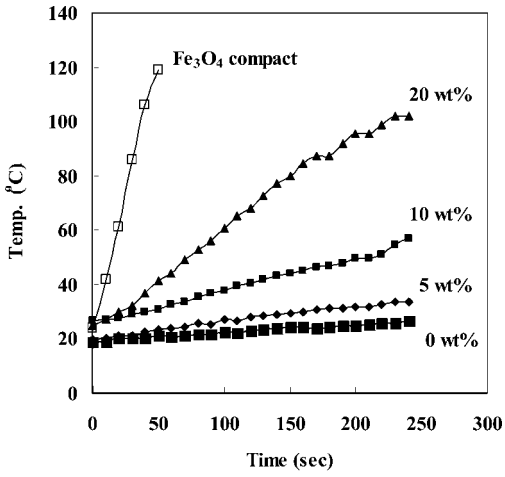

Figure 3. Temperature profiles under 80 W microwave irradiation of petalite foams containing different amounts of Fe_3O_4 which were previously sintered at 1200 °C.

stable oxide at high temperature. That Fe_3O_4 could be easily decomposed to α-Fe_2O_3 over 500 °C was confirmed by TG-DTA, and α-Fe_2O_3 was detected by XRD.

Temperature Profiles of the Composite Foam Using Microwave Irradiation. Figure 3 shows the temperature profiles under 80 W microwave irradiation for 240 s of some Fe_3O_4−petalite foams by self-heating. These foams were previously sintered at 1200 °C, i.e., prior to microwave irradiation. The Fe_3O_4 content in foams varied from 0 to 20 wt%. In Figure 3, the temperature profile of green compact plate (diameter, 40 mm; thickness, 5 mm; weight, 17 g; bulk density, 2.7 g/cm^3) is also shown as a reference. Fe_3O_4 green compact can absorb microwave energy well, and the surface temperature of the compact then rapidly reached 120 °C after 50 s, as expected.[1] Petalite ceramics are transparent to microwaves at room temperature, and the temperature of petalite foam was 27 °C after treatment for 240 s by microwave irradiation as shown in Figure 3 (0 wt % Fe_3O_4). By increasing the amount of Fe_3O_4, the composite foam could absorb microwaves and the temperature of 20 wt % Fe_3O_4−petalite foam reached around 100 °C after treatment for 240 s. The self-heating rates of 5, 10, and 20 wt % Fe_3O_4 foams were 0.05, 0.12, and 0.35 °C/s, respectively. Figure 4 shows the temperature profiles under 600 W microwave irradiation for 240 s of some foams, which were previously sintered at 1200 °C. Compared with the results of 80 W (Figure 3), the absorption of microwaves of 5 and 10 wt %

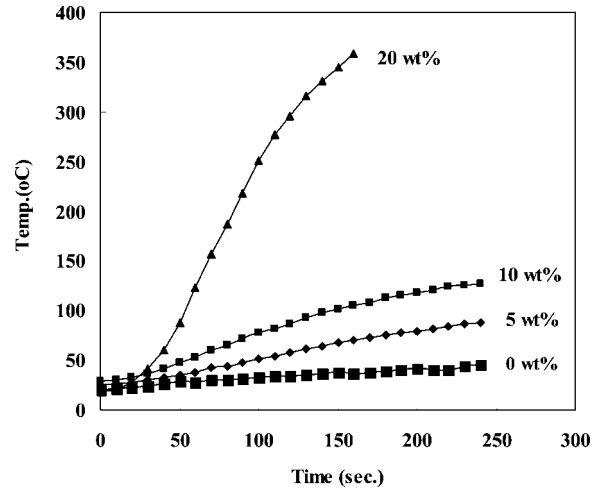

Figure 4. Temperature profiles under 600 W microwave irradiation of petalite foams containing different amounts of Fe_3O_4, which were previously sintered at 1200 °C.

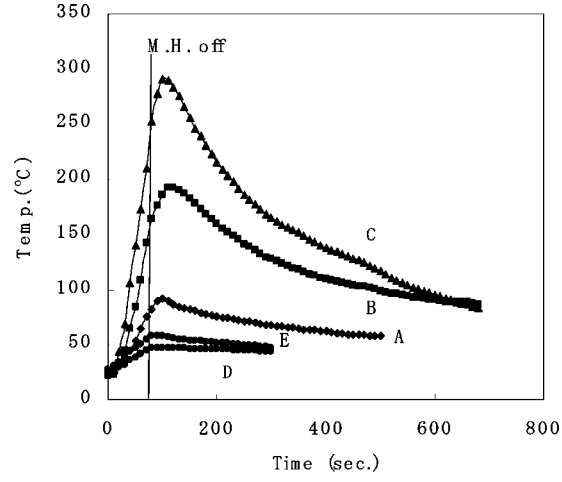

Figure 5. Heat energy holding ability of 20 wt % Fe_3O_4−80 wt % petalite composite plates sintered at 1100, 1150, and 1200 °C. Microwave power was 600 W and microwave heating (M-H) was cut off after 70 s: (A) 1100, (B) 1150, (C) 1200 °C, (D) commercial petalite ware sintered at 1200 °C without Fe_3O_4, and (E) commercial porcelain ware sintered at 1300 °C without Fe_3O_4.

Fe_3O_4 foams was promoted at 600 W (Figure 4), and the self-heating rates were 0.13 and 0.4 °C/s. In the case of 20 wt % Fe_3O_4, the microwave absorption was enhanced significantly after 20 s and the temperature reached 360 °C after treatment for 160 s (Figure 4), and the self-heating rate was about 3.0 °C/s.

Heat Energy Holding Ability of Fe_3O_4−petalite Plates. Novel plates of 20 wt % Fe_3O_4−80 wt % petalite were prepared successfully by sintering at 1100, 1150, 1200 and 1230 °C for 2 h. Figure 5 shows the heat energy holding ability of 20 wt % Fe_3O_4−-petalite plates sintered at 1100, 1150, and 1200 °C and the results are compared with two commercial wares. In this experiment, microwave power was 600 W, which was cut off after 70 s using the modified domestic microwave oven. Surface temperature increased linearly with the microwave irradiation time. The self-heating rates of the composites sintered at 1100, 1150, and 1200 °C were 0.9, 2.0, and 3.3 °C/s, respectively. After cutting off microwaves, the increase in temperature continued for 30−40 s, and the maximum temperatures of these samples were 84,

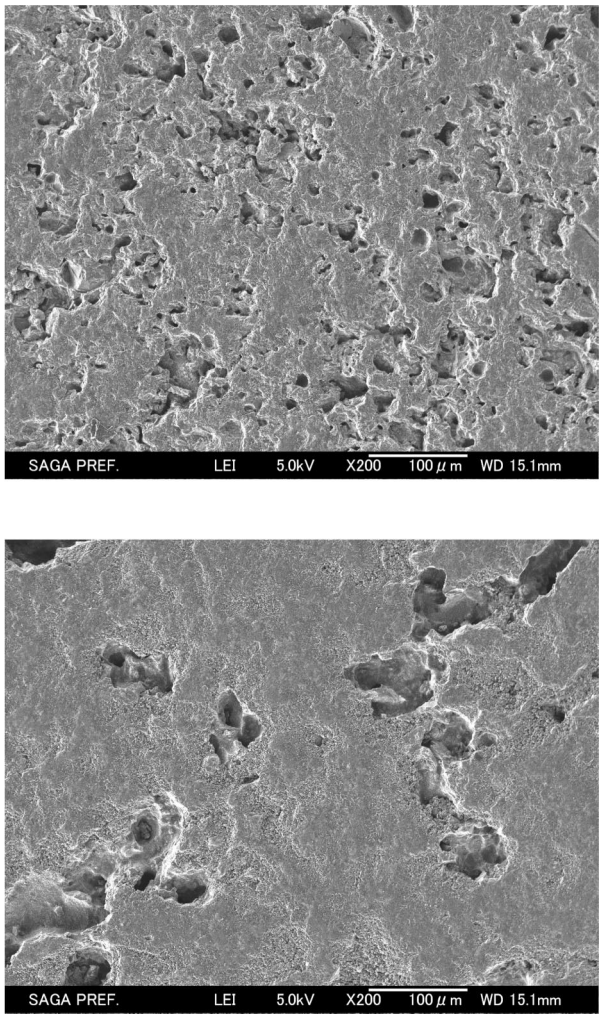

Figure 6. Microstructure of 20 wt % Fe_3O_4−80 wt % petalite composite plates sintered at (a) 1100 and (b) 1200 °C for 2 h.

Table 1. Porous and Thermal Properties of 20 wt % Fe_3O_4−petalite Composite Plates Sintered at 1100−1230 °C for 2 h, and Two Commercial Wares

sintering temp. (°C)	bulk density (g/cm^3)	porosity (%)	thermal expansion coefficient ($\times 10^{-6}$/°C)
1100	1.97	22.4	2.21
1150	2.14	14.8	2.48
1200	2.3	7.6	2.64
1230	2.38	5.8	3.05
commercial ware (1)	1.86	8.5	1.97
commercial ware (2)	2.34	4.7	6.81

197, and 294 °C. After that, temperature gradually decreased, and the final temperatures of the samples sintered at 1150 and 1200 °C were around 80 °C for 680 s. The final ambient temperature of the microwave oven was 70−74 °C, and both temperatures of the sample and ambient of the oven converged to the same temperature. The two commercial wares used for comparison did not heat up or retain heat in the same fashion as the novel 20 wt % Fe_3O_4−petalite composite plates (Figure 5).

From the above results, 20 wt % Fe_3O_4−80 wt % petalite composite plates have been discovered to have relatively high heat energy holding ability. Figure 6 shows the microstructure and Tables 1 and 2 show bulk density, porous, and thermal properties of 20 wt % Fe_3O_4−80 wt % petalite plates

Table 2. Thermal Properties of 20 wt % Fe_3O_4−petalite Composite Plates Sintered at 1100−1230 °C for 2 h, and Two Commercial Wares

sintering temp (°C)	specific heat J/(°C g)	thermal diffusivity (cm^2 s)	thermal conductivity (W/(m K))
1100	0.8149	0.003441	0.547
1150	0.8477	0.002887	0.524
1200	0.7534	0.003306	0.571
1230	0.8173	0.003608	0.596
commercial ware (1)	0.7596	0.002909	0.459
commercial ware (2)	0.7719	0.008131	1.521

Table 3. Removal Test of the Commercial Cooking Oil Coated onto 20 wt % Fe_3O_4−petalite Composite Plates Sintered at 1200 °C Using 600 W Microwave Irradiation.

irradiation time (s)	power of M.W. (W)	removal rate (%)	temp of plate (°C)
0	600	0	26
30	600	19.6	148
60	600	36.8	225
90	600	81.8	490 − 520[a]
120	600	98.1	710 − 750[a]
150	600	98.5	805 − 825[a]

[a] Temperature was measured by infrared pyrometer.

sintered at 1100−1230 °C. The composite samples sintered at 1100 °C had porous structure with 1.97 g/cm^3 bulk density and 22.4% porosity (Figure 6a), and the density increased i.e., porosity decreased with higher sintering temperatures (Figure 6b; Table 1). Thermal expansion coefficient of the composite changed from 2.21 to 3.05 $\times$ 10^{-6}/°C with sintering temperature due to densification (Table 2). The relatively low thermal expansion coefficients suggest that these ceramics could be used under the rapid heating and cooling conditions of microwave irradiation (for example, oil decomposition; see below). These ceramics have thermal expansion coefficients, which are only slightly higher than those of commercial petalite wares sintered at 1150−1200 °C (1.0−2.5 $\times$ 10^{-6}/°C)[19] (see also Table 1) because of the presence of α-Fe_2O_3 (8.0 $\times$ 10^{-6}/°C).[20] Specific heats, thermal diffusivity, and thermal conductivity of the composites sintered at 1100−1230 °C are reported in Table 2. By increasing the firing temperatures, the thermal conductivity of the composites increased because of densification. The results presented here reveal that the self-heating rate was strongly influenced by the sintering temperature (Figure 5) and the heat holding ability was influenced by low thermal conductivity (Table 2).

Here we also demonstrate the rapid removal of commercial cooking oil coated onto the composite plate by microwave irradiation (Table 3). A part of the oil was evaporated upon heating for 60 s in the temperature range of 120 to 225 °C. During microwave irradiation, the center area (about 1 cm^2) of the plate was locally red heated after 100 s, and the burning out or thermal decomposition of oil was enhanced. The removal rate was 98% after 120 s (Table 3). From this basic experiment, it will be expected that the waste organic contaminants could be rapidly decomposed or removed from microwave absorbing ceramic substrates by continuous microwave irradiation. The rapid thermal decomposition of harmful organic molecules using

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microwave irradiation is expected as one of the energy saving and environmentally benign remediation processes when done in a closed reaction system.[21]

Conclusions

Foams and plates made from a mixture of Fe_3O_4 and petalite mineral have been discovered to get rapidly heated under microwave irradiation and have relatively high heat energy holding ability compared to the presently used commercial ceramics. The $Fe_2O_3-Li_2O-SiO_2-Al_2O_3$ composition is ideally suited for microwave heating. The Fe_3O_4 component, which was transformed to Fe_2O_3 is responsible for microwave-assisted rapid self-heating of the composites and the relatively low thermal conductivity of these composites leads to their high heat holding ability. These novel ceramics, which could be rapidly heated by microwave irradiation, are being commercialized as microwave ware.

Supporting Information Available: Heat retaining ceramic plates made from a mixture of Fe_3O_4 and petalite mineral, rice cooker made from a mixture of Fe_3O_4, and petalite mineral being used in a microwave oven and modified domestic microwave oven for self-heating of Fe_3O_4−petalite foam composite (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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