Intelligent Reactions of Inorganic Phosphor Materials with Microwave Heating

Kazuyoshi Uematsu, Kenji Toda,† and Mineo Sato
Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2 8050, Niigata, 950-2181
†*Graduate School of Science and Technology, Niigata University, Ikarashi 2 8050, Niigata, 950-2181*

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$YVO_4:Eu^{3+}$ and $Mg_2SnO_4:Mn^{2+}$ phosphors were prepared using a domestic microwave oven. The temperature of the raw materials irradiated with a microwave was rose up to 1111–1716 K within 150 s, followed by a sharp drop in the temperature in spite of irradiating the microwave continuously. A low dielectric loss factor of the reaction products caused the sharp drop in temperature as soon as the reaction was completed.

There are several advantages in microwave heating compared with conventional heating techniques, in view of potentials for energy saving and shorter processing time, improved product uniformity and yields, improved or unique microstructures and properties, and formations of new materials. Recently, there have been growing interests in the use of the microwave heating for synthesis of inorganic compounds such as metal oxides,[1–3] chalcogenides,[4–6] oxide superconductors,[7,8] nitrides,[9] nanomaterials,[10–13] and metal halides.[14]

In the microwave heating, at least one component which is a good microwave absorber should be contained in starting raw materials in order to obtain enough high temperature to start a reaction. Temperature vs time profiles for materials irradiated by microwaves can be classified into two types.[15] In the first type, the temperature of the material increases rapidly upon the exposure of the microwave. The second type profile involves a gradual increase in temperature on the microwave exposure, followed by a "triggering point" at which the material temperature increases rapidly as in the case of the first type. The rapid increase in temperature in both cases is mostly related to the increase in dielectric loss tangent of the material. Therefore, in syntheses of inorganic materials using the microwave heating, experimental conditions should be severely controlled because a slight excess of microwave power or irradiation time would cause melting or decomposition of the products.[2,7,16]

In this letter, we have reported a self-consistently completed solid-state reaction for syntheses of $YVO_4:Eu^{3+}$ and $Mg_2SnO_4:Mn^{2+}$ phosphors using a microwave heating. In this reaction, the temperature of the products was automatically decreased in spite of continuous microwave irradiation as soon as the formation reaction was completed.

Powders of the relevant oxides, Y_2O_3, V_2O_5, and Eu_2O_3 or MgO, SnO_2 and MnO, were used as raw materials for the preparation of phosphor samples of YVO_4:Eu (5 mol %) and Mg_2SnO_4:Mn (0.5 mol %), respectively. The powders were weighed in an appropriate ratio and milled together in a ball mill. A fraction of the mixed powder (2.0 g) was pelletized with the dimensions of 15 mm in diameter and about 4 mm in thickness. In order to reduce an escape of heat from the surface of the pellet, the pellet was surrounded by the mixed powder (1.0 g). The sample was then placed in an insulator vessel made of silica wool. A thermocouple sheathed in a stainless steel was contacted to the surface of the sample pellet to monitor temperature change of the sample. In the synthesis of $Mg_2SnO_4:Mn^{2+}$, the insulator vessel was placed in a quartz tube where Ar gas was flowed at a rate of 8.3 $cm^3 \cdot s^{-1}$. A domestic microwave oven (2.45 GHz, RE-T55, Sharp Corp.) with power rates of 500 and 175 W was used for the present study. An inhomogeneous distribution of electromagnetic field density existed in the domestic microwave oven because of its multimode microwave type in the cavity. Thus, the highest density position (position A) of electromagnetic field was found prior to the experiment. A powder X-ray diffractometer (XRD, MXLabo, Mac Science) using Cu Kα radiation was employed to identify the crystalline phase of the synthesized materials. The dielectric properties of individual components of starting oxides and products were measured by a network analyzer (Hewlett Packard 8753A) equipped with a dielectric probe kit (Hewlett Packard 85070B) for the measurement at 298 K and with an open ended coaxial probe made of stainless steel for the measurement at 1073 K.

Figure 1 shows the temperature profile of the raw materials for synthesis of $YVO_4:Eu^{3+}$ at position A of the domestic microwave oven operated at 500 W. When the microwave power was supplied, the temperature went up to 1111 K within 150 s, followed by a sharp drop in temperature in spite of irradiating microwave continuously. The product was slightly sintered and accompanied with its color change from yellow to white. The product showed a strong red fluorescence due to Eu^{3+}.

Figure 2a shows the temperature profiles of the raw materials for synthesis of $Mg_2SnO_4:Mn^{2+}$ at position A in the microwave oven operated at 500 W. The temperature went up to 1577 K in 220 s, but no sharp drop in temperature was observed until the microwave power was turn off. When the microwave power was reduced to 175 W (Figure 2b), the highest temperature reached was only 663 K in 400 s, giving an insufficient formation reaction. These results indicate that 500-W power is too high and 175-W power is too low for the synthesis of

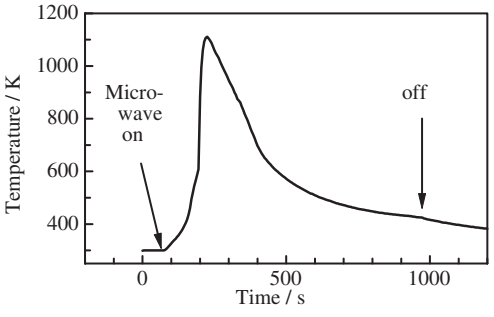

Figure 1. Microwave heating profile of mixture of Y_2O_3, V_2O_5, and Eu_2O_3.

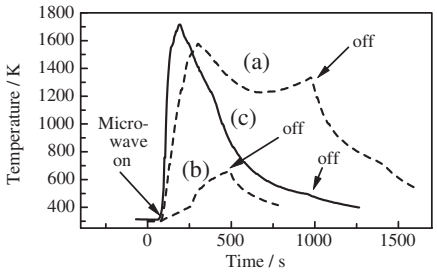

Figure 2. Microwave heating profiles of mixture of MgO, SnO_2, and MnO placed at position A operated at 500 W (a), placed at position A operated at 175 W (b), and at 10 mm higher than position A operated at 500 W (c).

$Mg_2SnO_4:Mn^{2+}$. Figure 2c shows the temperature profiles of the raw materials placed at the 10-mm higher position than position A to obtain slightly reduced microwave energy in the oven operated at 500 W. In this case almost the same temperature profile was obtained as that of $YVO_4:Eu^{3+}$ in Figure 1. The product showed a green fluorescence due to Mn^{2+}.

The XRD patterns of the products of $YVO_4:Eu^{3+}$ and $Mg_2SnO_4:Mn^{2+}$ are given Figures 3a and 3b, respectively. These products were single phases of the target materials.

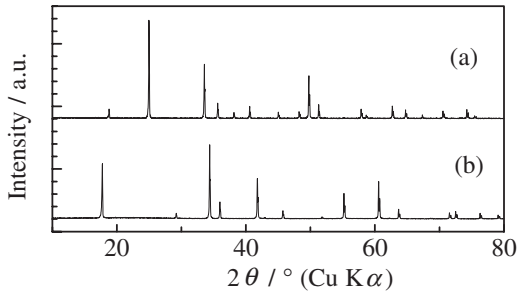

Figure 3. X-ray powder diffraction patterns of YVO_4:Eu (5 mol %) (a) and Mg_2SnO_4:Mn (0.5 mol %) (b) synthesized with microwave heating.

Generally, the energy absorbed by a material upon microwave irradiation is proportional to the dielectric loss factor, ε''_r, of the material, expressed by

$$\varepsilon''_r = \varepsilon'_r \cdot \tan\delta \quad (1)$$

where ε'_r is the relative dielectric constant and tan δ is the dielectric loss tangent, which is dependent on temperature of the material strongly. Table 1 shows values of ε''_r for the raw materials and the products measured at 2.45 GHz. Among all materials measured, only two materials, V_2O_5 and SnO_2, showed relatively high dielectric loss factors more than 0.2. These materials also showed a rapid increase in temperature to 1500 K within 30 s after microwave irradiation. These results confirmed that V_2O_5 and SnO_2 are good microwave absorbers at 298 K, providing an initial rapid rise in temperature to the starting raw materials. Contrarily, the products of $YVO_4:Eu^{3+}$ and $Mg_2SnO_4:Mn^{2+}$ are not good microwave absorbers because of its low ε''_r even at temperatures as high as 1073 K.

From these results, the temperature vs. time profile as shown in Figure 1 can be explained as follows. The mixture of the raw materials is first heated owing to the microwave absorption by V_2O_5 with large dielectric loss factor. Secondly, sufficiently high temperatures given by the microwave absorption afford to react V_2O_5 and Eu_2O_3 with Y_2O_3 to yield $YVO_4:Eu^{3+}$. Finally, low microwave absorption efficiency of the $YVO_4:Eu^{3+}$ product causes a rapid drop in the sample temperature. In the case of $Mg_2SnO_4:Mn^{2+}$ synthesis, the above mechanism could be true.

Table 1. Relative dielectric loss factor ε'' of raw materials and products at 2.45 GHz

Materials	at 298 K	at 1073 K
Y_2O_3	<0.1	0.3
V_2O_5	0.2	1.9[a]
Eu_2O_3	<0.1	—
$YVO_4:Eu^{3+}$ (Product)	<0.1	0.3
MgO	<0.1	<0.1
SnO_2	0.5	38.5
MnO	<0.1	—
$Mg_2SnO_4:Mn^{2+}$ (Product)	<0.1	<0.1

[a] This value is at 823 K, because melting point of V_2O_5 is 963 K.

In view of energy saving synthetic method, an ideal system is the one where the heating ceases spontaneously as quickly as the reaction is complete. The system proposed in this study could be the case, and called intelligent reaction system.

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