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Characterization of $YVO_4:Eu^{3+}$ phosphors synthesized by microwave heating method

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Abstract

$YVO_4:Eu^{3+}$ phosphors were prepared using a domestic microwave oven operated at 2.45 GHz with 500 W. The temperature of raw materials with mixtures of Y_2O_3, V_2O_5 and Eu_2O_3 that were irradiated with the microwave increased to about 840 °C within 150 s. Subsequently, the temperature dropped sharply in spite of the continuing microwave irradiation. Measurement of the dielectric loss factor of the raw materials and products at 2.45 GHz at temperatures from 25 °C to 800 °C revealed a high absorption efficiency of microwave energy by V_2O_5, which provided a rapid increase in the raw material's temperature. A low dielectric loss factor observed for YVO_4:Eu engendered a sharp temperature drop after completion of the reaction of Y_2O_3 with V_2O_5.

Keywords: Phosphors; Microwave heating; YVO_4:Eu; Luminescence; Dielectric loss factor

1. Introduction

Application of microwave heating technique to inorganic materials technology has been advanced for sintering and joining of ceramics [1]. Several advantages exist in microwave heating compared to conventional heating techniques. Although microwave heating requires less energy and processing time, it provides improved product uniformity and yields along with improved or unique microstructures and properties; moreover, it allows synthesis of new materials.

Recently, there has been growing interest in the use of the microwave heating for synthesis of inorganic compounds such as metal chalcogenides [2–4], oxide superconductors [5,6], nitrides [7], metal halides [8], and cathode materials for lithium ion batteries [9–11]. Peelamedu et al. employed a two-phase system in which two materials with different microwave absorption efficiencies were used to produce an anisothermal reaction [12]. That study obtained intermediate products that could not be synthesized by conventional heating reactions.

In microwave heating techniques, at least one component that is a good microwave absorber should be contained in starting raw materials to obtain sufficiently high temperatures to start a reaction. Temperature vs. time profiles for materials irradiated by microwaves can be classified into two types [1]. In the first type, the material temperature increases rapidly upon microwave exposure. The second type of profile involves a gradual increase in temperature upon microwave exposure, followed by a "trigger 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 the dielectric loss tangent of the material. Therefore, for syntheses of inorganic materials using microwave heating, experimental conditions must be controlled strictly because a slight excess of microwave power or irradiation time might cause product melting or decomposition [5,11,13].

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Lanthanide-doped yttrium orthovanadate (YVO_4:Ln) is a promising matrix for lamps, lasers, TV phosphors, plasma display panel (PDP) phosphors, etc. Therefore, many methods of YVO_4:Ln synthesis have been attempted, e.g., Pechini method [14], film formation by sol–gel processes [15,16], and formation of nanoparticles using hydrothermal reactions [17]. The authors have synthesized $YVO_4:Eu^{3+}$ and $Mg_2SnO_4:Mn^{2+}$ phosphors using 2.45 GHz microwave irradiation [18,19]. $YVO_4:Eu^{3+}$ phosphors synthesized by the microwave heating method had well-dispersed particles (2–3 μm diameter) without sintering and with higher homogeneous distribution of the Eu dopant in YVO_4 matrix compared with those synthesized by the conventional method [19].

This paper reports a self-consistently completed solid state reaction for syntheses of $YVO_4:Eu^{3+}$ phosphors using microwave heating. In this reaction, the product temperature decreased automatically in spite of continuous microwave irradiation as soon as the formation reaction was completed. Changed temperature profiles of raw materials irradiated with microwave are discussed in terms of dielectric properties of raw materials and the products at high temperatures.

2. Experimental

Powders of the relevant oxides, Y_2O_3, V_2O_5 and Eu_2O_3, were used as raw materials to prepare $YVO_4:Eu^{3+}$ phosphor samples. The powders were weighed appropriately and milled together in a ball mill with an agate ball using an agate container. A fraction of the mixed powder (2.0 g) was pelletized to 15 mm diameter and ca. 4 mm thickness. The pellet was surrounded by 1 g of mixed powder to reduce the escape of heat from the pellet surface. The sample was then put in an insulating vessel made of silica wool. The insulator box was placed in a domestic microwave oven (RE-T55; Sharp Corp.) operated at 2.45 GHz. Microwave irradiation was carried out at an electric power of 500 W for 15 min. A thermocouple sheathed in stainless steel was used to control and monitor the sample temperature. The thermocouple end was contacted to the center of the sample pellet surface covered with sample powder to correctly measure the sample temperature. For pellet temperature control, we used a temperature control system equipped with a solid state relay. A personal computer recorded the sample temperature every 5 s.

The products were analyzed using powder X-ray diffraction (XRD) on an X-ray diffractometer (MXLabo; Mac Science Ltd.) using Cu Kα radiation. Excitation and emission spectra were measured at room temperature for the powder sample using a spectrofluorometer (FP-6500; Jasco Inc.).

Dielectric properties of individual components of the starting oxides and products were measured using a network analyzer (8753A; Hewlett-Packard) equipped with a dielectric probe kit (85070B; Hewlett-Packard) at 25 °C and with an open ended coaxial probe at greater than 100 °C. The tailored open-ended coaxial probe was made of stainless steel. The outer diameter of the center conductor and the inner diameter of the outer conductor were 3.5 mm and 8.5 mm, respectively. The probe was 290 mm long. At high temperatures, 0.1 g quartz wool was used as an insulator in the probe.

3. Results and discussion

3.1. Phosphor preparation

Fig. 1 shows temperature profiles of the raw materials, whose temperature was controlled to 500 °C, 600 °C and 800 °C upon irradiation of microwaves operated at 500 W. In all cases, the temperatures increased drastically upon irradiation. After this rapid temperature increase, the temperature was well controlled in the case of 500 °C. In the other two cases, although the ambient temperature increased to around the target temperature, a sharp temperature drop occurred in the sample in spite of the irradiating microwave.

Fig. 2a shows the temperature profile of the raw material without temperature control. When microwave power was supplied, the temperature immediately increased to 838 °C within 150 s. A sharp temperature drop followed despite continuous irradiating microwaves. The product was sintered slightly and its color changed from yellow to white. The product showed strong red fluorescence from Eu^{3+} upon exposure to 254 nm ultraviolet light. This phosphor material was irradiated again: the resultant temperature profile is shown in Fig. 2b. Different from the case of the fresh starting material, the temperature increase upon microwave exposure was quite slow, increasing the temperature to about 200 °C after 900 s exposure.

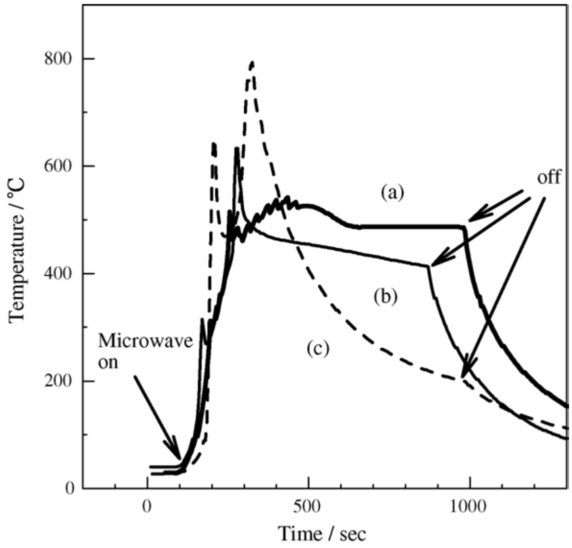

Fig. 1. Microwave heating profiles of a starting mixture of Y_2O_3, V_2O_5 and Eu_2O_3, temperature-controlled at (a) 500 °C, (b) 600 °C, and (c) 800 °C.

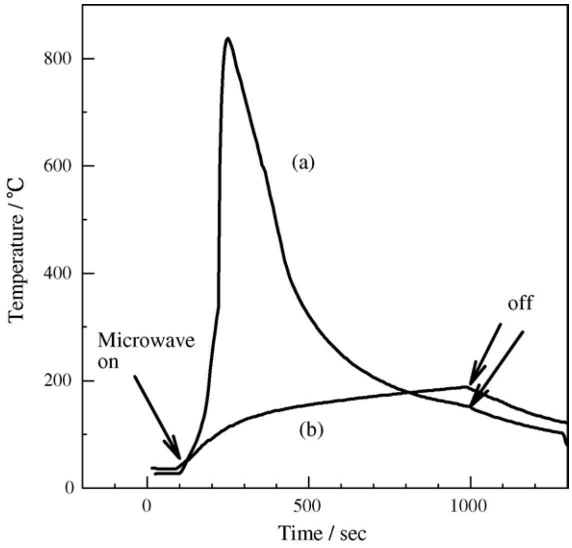

Fig. 2. Microwave heating profiles of (a) a starting mixture of Y_2O_3, V_2O_5, and Eu_2O_3 and (b) a YVO_4 product. Neither case was temperature-controlled.

The products' XRD patterns are shown in Fig. 3. The XRD pattern of the sample obtained by a conventional furnace heating method at 1100 °C for 4 h is also given in Fig. 3 for comparison. In cases that were temperature-controlled at 500 °C, 600 °C and 800 °C, the products were contaminated with the raw material of Y_2O_3 as a minority phase. On the other hand, a single phase of the target material was obtained by microwave heating without temperature control. These results confirm that microwave irradiation without temperature control provides a satisfactory condition for formation of the single phase of YVO_4 within the short time of 900 s.

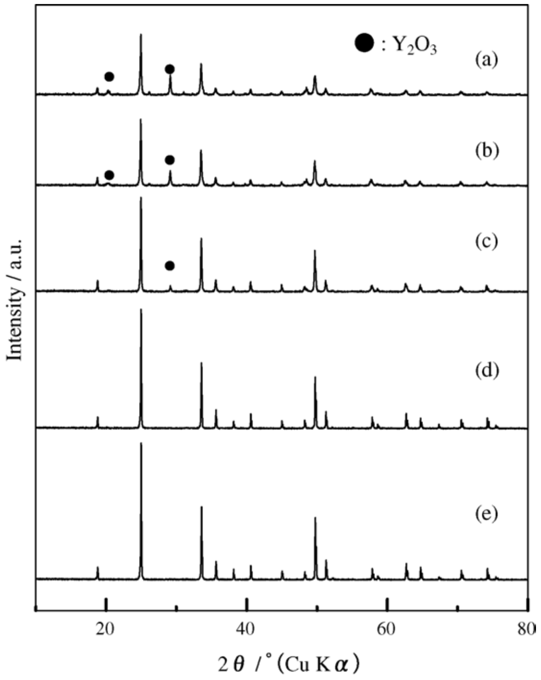

Fig. 3. XRD patterns of heated materials (a) temperature-controlled at 500 °C, (b) temperature-controlled at 600 °C, (c) temperature-controlled at 800 °C, (d) without temperature control, and (e) at 1100 °C for 4 h by conventional solid state method.

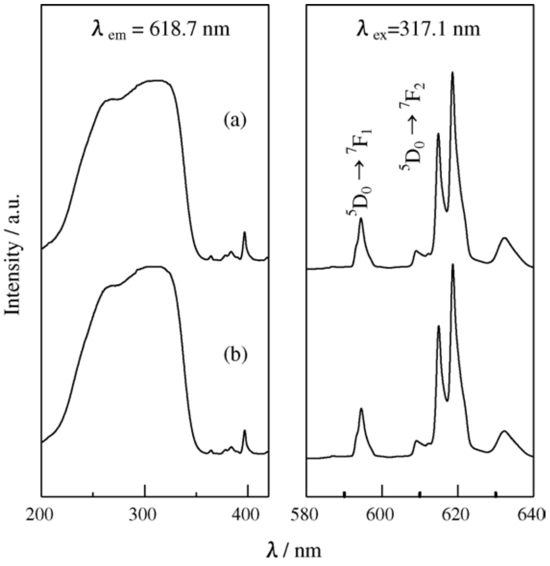

Fig. 4. Excitation spectra (λ_{em} = 618.7 nm) and emission spectra (λ_{ex} = 317.1 nm) for heated materials of (a) without temperature control and (b) using conventional solid state method (1100 °C, 4 h).

Fig. 4 shows excitation and emission spectra of the products obtained through microwave heating without temperature control and conventional heating. A broad excitation peak located at around 317 nm corresponds to absorption by the YVO_4 host crystal [20]. Emission peaks at around 610–630 nm result from the electric dipole transition of Eu^{3+} ($^5D_0 \rightarrow {^7F_2}$) induced by the lack of inversion symmetry at Eu^{3+} sites [21]. Emission spectra of the microwave-heated sample were almost as intensive as those of the sample obtained through conventional heating method.

3.2. Electromagnetic properties

The sharp drop in sample temperature (Fig. 2a) is attributable to drastic changes in dielectric properties of the product. The degree of microwave absorption by a dielectric material is related to the relative dielectric loss factor, ε_r', of the material, expressed as

$$\varepsilon_r'' = \varepsilon_r' \tan\delta, \tag{1}$$

where ε_r' is the relative dielectric constant and $\tan\delta$, the dielectric loss tangent; both are frequency-dependent. Fig. 5 shows the relative dielectric loss factors, ε_r'', for the V_2O_5, Y_2O_3 and YVO_4:Eu at 2.45 GHz measured in the temperature range of 25–800 °C. Low values of ε_r'' (<0.28) in the temperature range of 25–800 °C were observed for Y_2O_3 and YVO_4:Eu. In contrast, a relatively high ε_r'' value (0.4) at 25 °C was observed for V_2O_5; furthermore, the value became much higher (ε_r'' = 1.9) at 550 °C. These facts indicate that V_2O_5 is a microwave absorber that can provide increased temperature to the starting

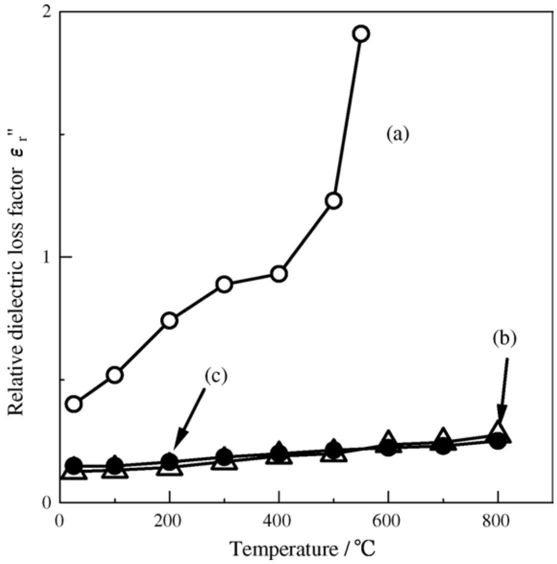

Fig. 5. Relative dielectric loss factors measured for (a) V_2O_5, (b) Y_2O_3, and (c) YVO_4:Eu.

material. Contrarily, the product of YVO_4:Eu^{3+} is not a good microwave absorber, as indicated by its low ε_r''.

These results suggest the following explanation of the temperature vs. time profile, as shown in Fig. 2(a). The raw material mixture is first heated by microwave absorption by V_2O_5 with a large dielectric loss factor. Secondly, a sufficiently high temperature given by microwave absorption engenders the reaction of V_2O_5 with Y_2O_3 to yield YVO_4. Finally, the decrease in microwave absorption efficiency of the YVO_4 product causes a rapid drop in the sample temperature.

4. Conclusions

YVO_4:Eu^{3+} phosphors were prepared using a domestic microwave oven operated at 2.45 GHz with 500 W. The temperature of the raw material, a mixture of Y_2O_3, V_2O_5 and Eu_2O_3, increased ca. 840 °C within 150 s after microwave exposure. Subsequently, the temperature dropped sharply in spite of continuous microwave irradiation. Measurement of the loss factor at 2.45 GHz shows that highly efficient absorption of microwave energy by V_2O_5 increased the temperature of the mixture. On the other hand, a low loss factor of the YVO_4 product caused a sharp temperature drop upon completion of the reaction of Y_2O_3 with V_2O_5. An ideal energy saving synthetic method system is one in which the heating eases spontaneously when the reaction is completed. The system proposed herein meets that criterion.

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