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Microwave synthesis of $LaCrO_3$

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The synthesis of $LaCrO_3$ from a stoichiometric mixture of Cr_2O_3 and La_2O_3 powder by microwave irradiation was examined using a multi-mode 28 GHz microwave heating system. In the La_2O_3–Cr_2O_3 system, Cr_2O_3 strongly absorbs microwaves while La_2O_3 is transparent to microwaves. The reaction proceeded rapidly and $LaCrO_3$ could be synthesised within 15 min of irradiation. Surprisingly, the temperature required for the microwave synthesis (440 °C) is much lower than that for conventional synthesis (> 1200 °C) using an electric furnace. The effect of the partial pressure of oxygen in the microwave chamber on the formation of $LnCrO_3$ was investigated. The formation of $LnCrO_3$ is enhanced with increase in the partial pressure of oxygen for Ln = La and Nd, while opposite behavior is seen for Ln = Gd, Tb, Dy and Ho.

1 Introduction

Lanthanum chromite, $LaCrO_3$, has received much interest as an electrode or interconnector for solid oxide fuel cells (SOFC) and a heating element for high-temperature electric furnaces.[1] Generally, $LaCrO_3$ is synthesised by solid state reaction of the component oxides at high temperatures ($T > 1200$ °C) in air. Since the diffusion of reactants is very slow in the solid state reaction, the reaction requires a long heating period and intermediate grinding to achieve good homogeneity. Attempts to synthesise $LaCrO_3$ at lower temperature have been made by hydrothermal reaction[2] and thermal decomposition of a mixed organometallic complex of La and Cr.[3]

Microwave heating has been used for the syntheses of various inorganic materials, *e.g.*, $YBa_2Cu_3O_{7-\delta}$,[4,5] La_2CuO_4,[5] β-SiC,[6] $BaWO_4$,[7] $Bi_4V_2O_{11}$, PbV_2O_6.[8] If some constituent materials of a chemical reaction system strongly absorb microwaves, the resulting heat generated can be used to drive a solid state reaction with another component. This is especially applicable for solid state reaction systems containing C, V_2O_5, Cr_2O_3, CuO, MnO_2, PbO_2, WO_3 or Fe_3O_4.[9] Detailed aspects of microwave processing have been reviewed by Sutton.[10]

The above mentioned examples were investigated by using microwaves with a frequency of 2.45 GHz which is widely applied for heating and cooking foodstuffs. It is known by experiment that the required size of the microwave chamber to achieve a uniform electric field distribution is directly proportional to the wavelength of the microwaves.[11]

The temperature rise of a material due to coupling with the microwaves is theoretically proportional to the dielectric loss factor of the material.[9] However, because the dielectric loss factor correlates with temperature and microwave frequency,[9] different temperature profiles may be obtained even for the same material if the frequencies of microwaves used are different.

Chromium sesquioxide (Cr_2O_3) absorbs 2.45 GHz microwave radiation very strongly.[12] If Cr_2O_3 absorbs 28 GHz microwave radiation in a similar manner, such microwaves can be utilised for the syntheses of various chromium double oxides. This paper reports the rapid and simple procedure for the synthesis of $LaCrO_3$ by 28 GHz microwave irradiation. The oxygen pressure dependence on the formation of $LnCrO_3$ (Ln = La, Nd, Gd, Tb, Dy and Ho) is also investigated.

2 Experimental

The increase in temperature of Cr_2O_3 and La_2O_3, and the possible synthesis of $LaCrO_3$ by microwave irradiation were determined. Multi-mode microwave heating equipment (Fuji Dempa Kogyo Co., LTD, Japan; FMS-10–28) was used. Appropriate amounts of Cr_2O_3 and La_2O_3 powder were mixed and pressed into a pellet (10 mm in diameter and 5 mm in thickness). A hole (1.6 mm in diameter and 3 mm in depth) was drilled at the centre of pellet to insert a thermocouple. In the microwave chamber (multi-mode cavity; 0.8 m in diameter and 1.2 m in length), a platinum sheathed Pt–Pt/Rh10% thermocouple (1.5 mm in diameter) was inserted into the sample pellet and then the sample was surrounded by quartz wool as a heat insulating material which is transparent to microwaves. A platinum sheath was used to achieve an effective shielding from the microwaves. A schematic illustration of the sample set up is shown in Fig. 1. The temperature was monitored during microwave irradiation. We considered that monitored temperature was not affected by microwave dielectric fields as suggested by Rowly *et al.*[13] After irradiation, the

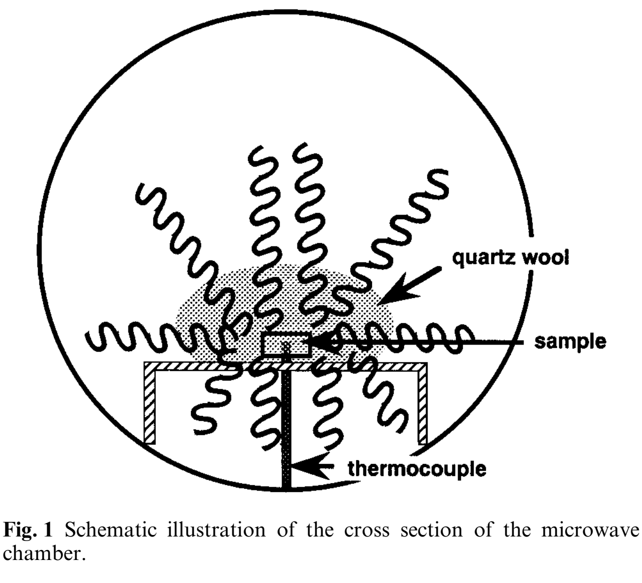

Fig. 1 Schematic illustration of the cross section of the microwave chamber.

sample was cooled to room temperature in the microwave chamber and the obtained sample was characterised by X-ray diffraction analysis and scanning electron microscopy.

3 Results and discussion

Fig. 2 shows the temperature–time profiles of (a)Cr_2O_3 and (b)La_2O_3 during 28 GHz microwave irradiation (0.3 kW output) in air. It is apparent that La_2O_3 is transparent to 28 GHz microwave radiation. In contrast to La_2O_3, the temperature of Cr_2O_3 rose rapidly. It was reported that the temperature of Cr_2O_3 rose rapidly above 1200 °C on exposure to a few minutes (referred to 'thermal runaway') of 2.45 GHz microwave irradiation.[12] However, the drastic temperature rise was completed within 2 min and the temperature stabilized at *ca.* 500 °C over longer periods of irradiation when 28 GHz microwaves was irradiated on Cr_2O_3. The difference is thought to be due to the difference in the dielectric properties of Cr_2O_3 at 28 GHz and 2.45 GHz. X-Ray diffraction analysis of the irradiated sample did not reveal any phase changes.

Fig. 3 shows the temperature–time profiles of a $Cr_2O_3 + La_2O_3$ stoichiometric mixture during 28 GHz microwave irradiation of (a) 0.3 kW, (b) 0.5 kW and (c) 1 kW in air. The profile of the $Cr_2O_3 + La_2O_3$ mixture is similar to that of Cr_2O_3 with the maximum temperature reached for the $Cr_2O_3 + La_2O_3$ mixture being slightly lower than that of Cr_2O_3. The profiles at various microwave power are quite similar except for differences in saturation temperature.

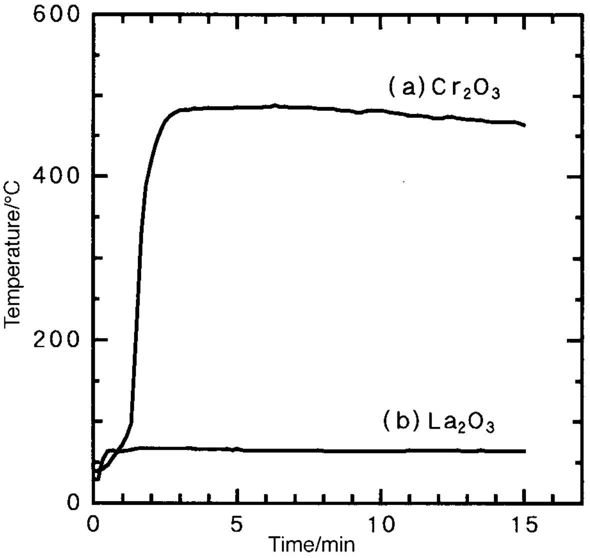

Fig. 2 Temperature–time profiles of (a) Cr_2O_3 and (b) La_2O_3 during 0.3 kW microwave irradiation in air.

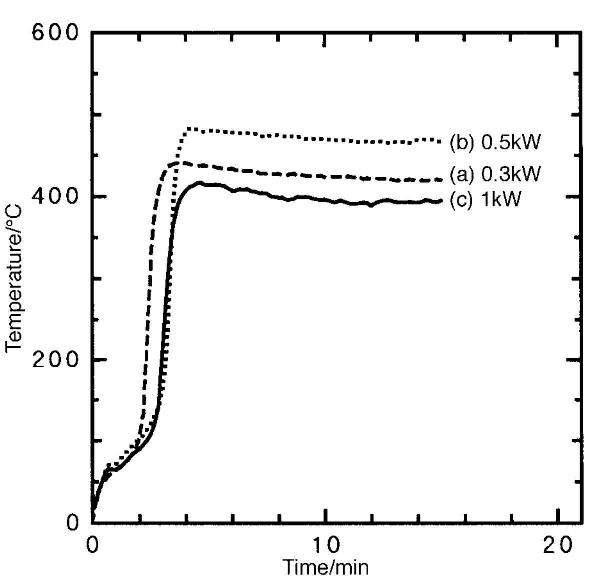

Fig. 3 Temperature–time profiles of $Cr_2O_3 + La_2O_3$ stoichiometric mixture during microwave irradiation of (a) 0.3 kW, (b) 0.5 kW and (c) 1 kW in air.

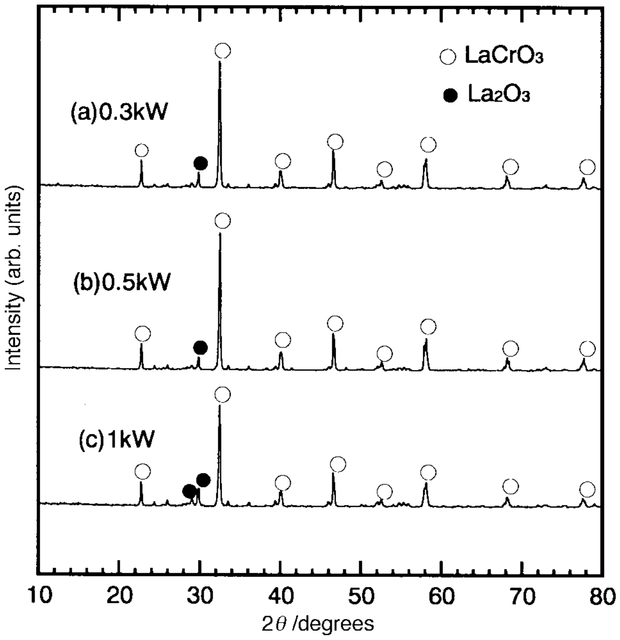

Fig. 4 X-Ray diffraction patterns of $Cr_2O_3 + La_2O_3$ stoichiometric mixture after microwave irradiation of (a) 0.3 kW, (b) 0.5 kW and (c) 1 kW in air.

X-Ray diffraction patterns of $Cr_2O_3 + La_2O_3$ mixtures after microwave irradiation of various power outputs (a) 0.3 kW, (b) 0.5 kW and (c) 1 kW in air for 15 min are shown in Fig. 4. As seen, $LaCrO_3$ was readily formed from a mixture of $Cr_2O_3 + La_2O_3$ within a short time (15 min) at each microwave power, but the amount of $LaCrO_3$ formed at 0.3 and 0.5 kW was slightly larger than that at 1 kW. This result is due to the

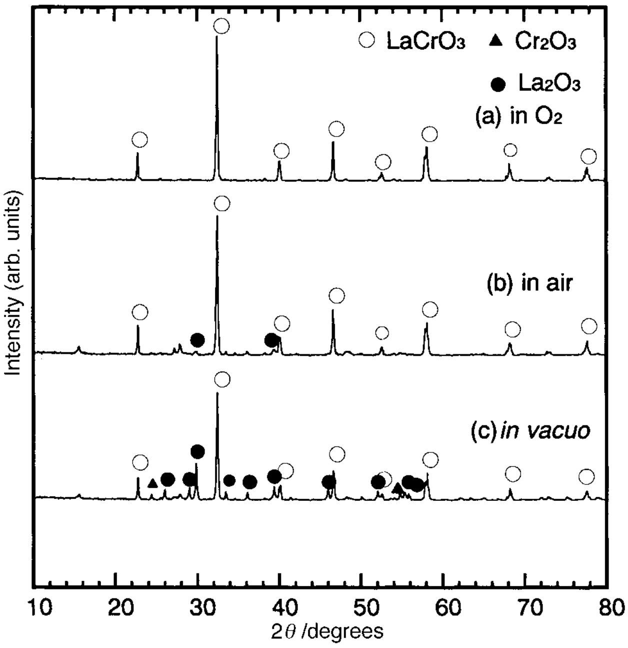

Fig. 5 X-Ray diffraction patterns of $Cr_2O_3 + La_2O_3$ stoichiometric mixture after 0.3 kW microwave irradiation (a) in O_2(3.7 atm), (b) in air and (c) *in vacuo*.

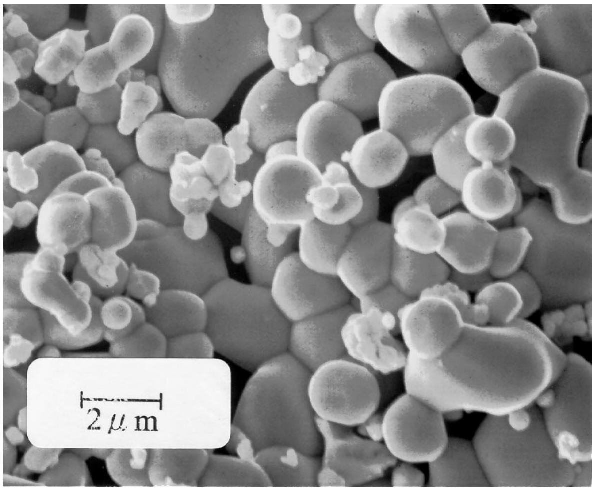

Fig. 6 Scanning electron micrograph of $LaCrO_3$ obtained by 0.3 kW microwave irradiation in O_2(3.7 atm) atmosphere.

difference in the maximum temperature at each microwave power and high microwave power is thus not required for the synthesis of $LaCrO_3$. It is notable that it takes only 15 min to synthesise $LaCrO_3$ by microwave irradiation, which is a very short time as compared with conventional heating methods.[14]

Fig. 5 shows the X-ray diffraction patterns of a $Cr_2O_3+La_2O_3$ mixture after 0.3 kW microwave irradiation (a) in O_2(3.7 atm), (b) in air and (c) *in vacuo* for 15 min. It can be seen that $LaCrO_3$ was formed in each atmosphere and the higher the partial pressure of O_2, the smaller was the amount of the unreacted La_2O_3 and Cr_2O_3. When the irradiation was carried out at a pressure of 3.7 atm oxygen, single phase $LaCrO_3$ was obtained. Generally, conventional synthesis of $LaCrO_3$ does not require a high oxygen pressure. Synthesis under high oxygen pressure leads to the formation of volatile chromium(VI) oxide.[15] However, in the microwave synthesis, chromium(VI) oxides was not formed even at 3.7 atm oxygen. This is due to considerably lower reaction temperature for the microwave synthesis as compared with the conventional synthesis.

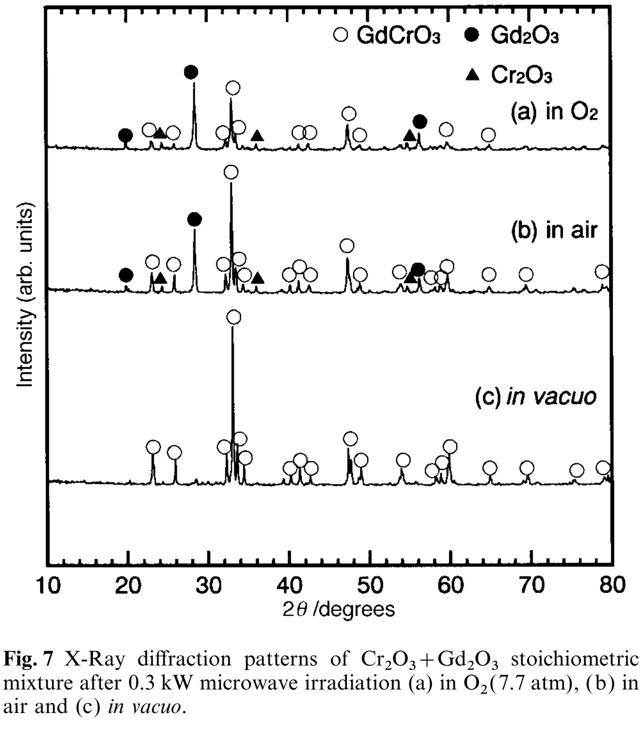

Fig. 7 X-Ray diffraction patterns of $Cr_2O_3+Gd_2O_3$ stoichiometric mixture after 0.3 kW microwave irradiation (a) in O_2(7.7 atm), (b) in air and (c) *in vacuo*.

Scanning electron microscopy showed that the particle size of the raw material powders, Cr_2O_3 and La_2O_3, were 0.39 and 0.79 μm, respectively. Fig. 6 shows a scanning electron micrograph of $LaCrO_3$ obtained by microwave heating. In this case, microwave heating was carried out using a 0.3 kW output in 3.7 atm oxygen pressure for 15 min. After microwave irradiation, the average particle size of the resultant $LaCrO_3$ was about 1.6 μm, with a size distribution of 0.4–3.2 μm.

The synthesis of other lanthanide chromites, $LnCrO_3$(Ln = Nd, Gd, Tb, Dy, Ho), from stoichiometric mixtures of Cr_2O_3 and Nd_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, or Ho_2O_3 have also been carried out. Fig. 7 shows the X-ray diffraction patterns of $Cr_2O_3+Gd_2O_3$ mixtures after 0.3 kW microwave irradiation for 30 min in various atmospheres. It is clear that $GdCrO_3$ was formed in each atmosphere. However, in contrast to $LaCrO_3$, the amount of $GdCrO_3$ increased with decreasing the partial pressure of oxygen and single phase $GdCrO_3$ was obtained *in vacuo*. During our extensive study, it was seen that the effect of the atmosphere on the formation of the $LnCrO_3$ phase by microwave irradiation can be divided into two groups *i.e.*, enhancement or inhibition of reactivity upon increasing the partial pressure of O_2. The former behavior is seen for $LaCrO_3$ and $NdCrO_3$, and the latter for $GdCrO_3$, $TbCrO_3$, $DyCrO_3$ and $HoCrO_3$. Considering the lanthanide contraction, we can suppose that it is easy to synthesise $LnCrO_3$ under high partial pressure of O_2 if the ionic radius of Ln is relatively large (Ln = La, Nd), while the use of a low partial pressure of O_2 is favoured if the ionic radius of Ln is relatively small (Ln = Gd, Tb, Dy, Ho). This difference must be due to differences in the diffusion mechanism for the formation of $LnCrO_3$ from a Ln_2O_3 and Cr_2O_3 mixture for different Ln. Although the detailed diffusion mechanism under microwave irradiation has, as yet, not been clarified, it should be pointed out that the difference in crystal structure of Ln_2O_3, *i.e.*, hexagonal A-type for Ln = La, Nd and cubic C-type for Ln = Gd, Tb, Dy and Ho, would affect the diffusion mechanism for the formation of $LnCrO_3$ *via* solid state reaction with Cr_2O_3.

In conclusion, a new simple procedure for the synthesis of $LaCrO_3$ has been developed in the present study. Microwave heating is effective for the synthesis of complex oxides containing a component oxide strongly coupled with microwaves. There is still an unsolved problem as to why the reaction proceeded rapidly and completely within a short time at low temperature (440 °C). This observation suggests an existence of a 'non-thermal effect' of the microwave electric field on diffusion of chemical species.

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