

High temperature dielectric study of Cr_2O_3 in microwave region

D. C. Dube,^{a)} D. Agrawal,^{b)} S. Agrawal, and R. Roy
Materials Research Institute, University Park, Pennsylvania 16802

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A unique cavity perturbation method has been used to study the dielectric behavior of chromium oxide (Cr_2O_3) in the microwave region at ~ 3.5 GHz and temperatures up to ~ 1100 °C. The specimen in the form of pellet was heated by microwave power at 2.45 GHz in e-field of a single mode cavity. In the temperature range of measurement, the dielectric constant is found to increase within 10% and loss factor within one and a half times the room temperature values. Results are discussed in the light of agitated ionic motion in the material. © 2007 American Institute of Physics. [DOI: 10.1063/1.2716336]

High corrosion and oxidation resistant properties of coatings of chromium oxide and its applications in industrial gas turbines and in steel manufacturing are well known. Besides being an excellent electrical insulator, it is one of the hardest oxide materials.¹ Chromium oxide is quite stable at normal oxygen pressures up to around 1400 °C.² In thin film form, this material has been shown to exhibit very attractive mechanical properties such as high adhesion and hardness.^{3–6}

In recent work, this laboratory has analyzed the products and the multiphoton laser (QQC) process which led to the production of these unique coatings (even 500 μm thick) of Cr_2O_3 on steel and stellite. These coatings applied to most metals, proved to be vastly more adherent than any similar coatings of a chemically soluble and ultrahard phase (Cr_2O_3 is harder than Al_2O_3 sapphire).⁷ Hence this family of Cr_2O_3 on metal coatings is a significant breakthrough in the coatings industry.

As we introduced the concept of multienergy processing into material processing, it became clear that an interesting case of genuinely distinct multienergy as distinct from “multiwavelength-multienergy” processing would be to combine a microwave field and a pulsed laser source. The first example of material interaction under these conditions was accomplished on ZrO_2 with an yttrium aluminum garnet laser and a multimode of 2.45 GHz microwave field.⁸ When Cr_2O_3 was substituted, the behavior of the oxide itself in the microwave field was proven to be very different indeed. That led us to study the phenomenon involved in more detail.

In order to study the high temperature dielectric behavior of materials in the gigahertz region, a technique was developed earlier.^{9,10} Using this technique, the changes in the complex permittivity of chromium oxide at 3.5 GHz up to a temperature around 1100 °C have been recorded and are presented here.

Commercially available chromium oxide (Alfa-Aesar, purity 99%) was used in the present study. Pellets (6 mm diameter, 2–3 mm thickness) were pressed and annealed at 1100 °C for 4 h in a conventional furnace in air.

Our measurement technique uses two microwave signals simultaneously coupled to the cavity made out of WR 340 rectangular waveguide. A high power (300–800 W) signal at

2.45 GHz heats the specimen, while a low power (a few milliwatt) signal from a network analyzer at ~ 3.5 GHz measures permittivity in the cavity. The reason for choosing different frequencies for measurement is to facilitate decoupling of the high power signal from the network analyzer. And this can be achieved by using two C-band waveguides C_1 and C_2 as filters, as shown in Fig. 1. The specimen can be located in maximum magnetic field for permeability studies¹⁰ or in maximum electric field for dielectric studies, as shown in Fig. 1. In the present case, the specimen was placed in maximum electric field in the cavity and the perturbation equations may be applied to get dielectric parameters.¹¹ It is, however, more convenient to study variations in these parameters as a function of temperature.

Thus, the changes in dielectric constant ($\Delta\epsilon'$) and changes in dielectric loss factor ($\Delta\epsilon''$), from basic perturbation equations, may be expressed as a function of temperature as^{9,10}

$$\Delta\epsilon'(T) = \frac{V_c [f_r(T_2) - f_r(T_1)]}{V_s 2f_s} \quad (1)$$

and

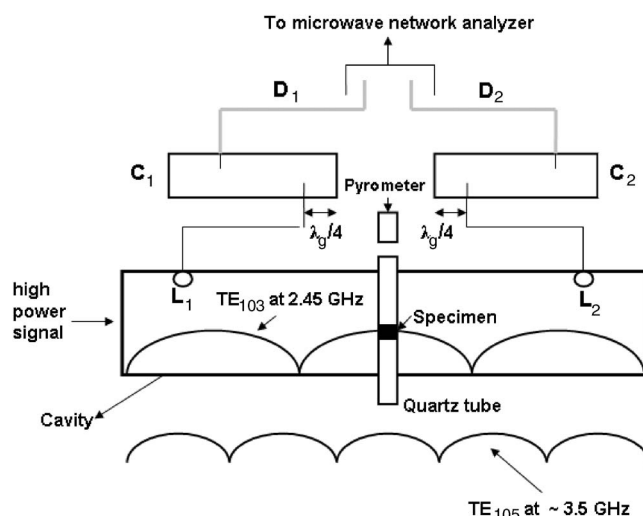


FIG. 1. Experimental setup: C_1 and C_2 are C-band rectangular waveguides used to decouple high power of 2.45 GHz signal from network analyzer. D_1 and D_2 are connecting 50 Ω cables. (Ref. 9). λ_g refers to 3.5 GHz. The coaxial loops L_1 and L_2 are located in the cavity at magnetic field maxima for TE_{105} mode. The other ends of L_1 and L_2 are connected to the network analyzer through two C-band waveguide filters.

^{a)}Formerly at: Physics Department, Indian Institute of Technology-Delhi, India.

^{b)}Author to whom correspondence should be addressed; electronic mail: dxa4@psu.edu

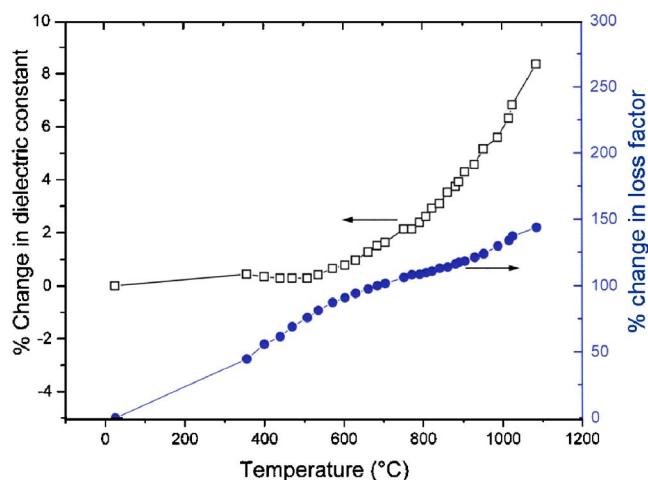


FIG. 2. (Color online) Changes in dielectric constant and loss factor with temperature for chromium oxide at 3.5 GHz.

$$\Delta\epsilon''(T) = \frac{V_c}{4V_s} [Q_s^{-1}(T_2) - Q_s^{-1}(T_1)], \quad (2)$$

where V_c and V_s are volumes of cavity and the specimen, respectively, $f_r(T_1)$ represents the resonance frequency of the cavity (with specimen) at specimen temperature T_1 (say, room temperature), and $f_r(T_2)$ is the resonance frequency at higher temperature T_2 . $Q_s(T_1)$ is the quality factor ($=f_r/\text{BW}$) where BW represents 3 dB bandwidth of resonance peak at temperature T_1 and $Q_s(T_2)$ the quality factor at temperature T_2 . f_s represents the resonance frequency of the cavity when it contains the specimen at room temperature. The resonance parameters of the copper cavity itself are assumed invariant with temperature in writing Eqs. (1) and (2).

Other parameters being constant, Eqs. (1) and (2) suggest that change in the dielectric constant ϵ' is proportional to the change in resonance frequency f_r , and change in dielectric loss factor ϵ'' is proportional to the change in 3 dB bandwidth of the resonance peak. Thus by recording these changes, dielectric behavior of the materials may be studied as a function of temperature. These parameters were obtained using a Hewlett Packard vector network analyzer (model 8753E).

The dielectric behavior of Cr_2O_3 as a function of temperature up to $\sim 1100^\circ\text{C}$ is illustrated in Fig. 2, where ϵ' and ϵ'' are expressed as percent change. The experimental points from room temperature to 370°C are missing because the digital infrared pyrometer (Raytek, Model: RAYMA2SCCF) used starts reading from 350°C .

The extent of change in dielectric constant is estimated from Eq. (1). Thus a shift of 100 kHz in resonance frequency at 3.5 GHz amounts to a change in ϵ' of ~ 0.13 , the cavity to sample volume ratio being about 9000. Taking a room temperature value of ϵ' for Cr_2O_3 as 10.3, the percent change $\Delta\epsilon'$ has been deduced and shown in Fig. 2.

The dielectric loss factor for Cr_2O_3 at room temperature was found to be $\sim 2.5 \times 10^{-3}$, it being proportional to 3 dB bandwidth of the resonance curve [Eq. (2)] in Fig. 2, the variation of loss factor with temperature has been plotted as the percent change with respect to room temperature value.

The dielectric constant remains constant within the limits of accuracy of measurements up to $\sim 550^\circ\text{C}$ and then starts rising with increasing temperature. From 800°C on-

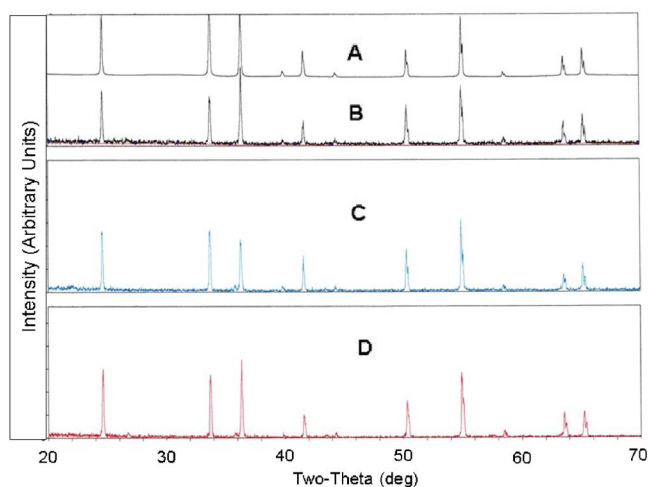


FIG. 3. (Color online) X-ray diffraction patterns of the Cr_2O_3 samples: (A) processed in conventional furnace at 1100°C for 4 h, (B) unprocessed, (C) processed in microwave E field at 1100°C , and (D) processed at 900°C in E field. All patterns are almost identical indicating no compositional changes.

wards, the rise is rather fast. Dielectric loss, in general, is more sensitive to temperature. The loss increases almost linearly up to 600°C . However, this rise is slowed down between 600 and 900°C and seems to pick up again. It may be mentioned here that the specimen is in the quartz tube in the cavity. The section of the tube containing specimen also gets heated up with the specimen and may make a contribution (though small) to these measured losses.

The dielectric results depicted in Fig. 2 seem to represent a typical example of intrinsic behavior of ionic solids at high temperatures. Accordingly, the increasing trend in dielectric parameters can be understood to a large extent in terms of increasing contributions from ion migration at elevated temperatures. The contributions from ion vibrations and deformation losses, though apparently low, may not be negligible particularly due to high heating rates encountered in the microwave field. These processes may initiate strong molecular agitation. In addition to the above, contributions to dielectric losses from grain boundaries may also not be negligible.

The dielectric patterns recorded on two pellets of different thicknesses were the same, thus any influence of geometrical parameters on the measurements was ruled out. To look for any compositional changes during microwave heating, x-ray analysis was performed on pellets before and after microwave heating, and also on another sample quenched after heating in cavity at 900°C . The results given in Fig. 3 indicate the absence of any substantial compositional changes.

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