On the changes and reactions in metal oxides under microwave irradiation

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Metal oxides are the starting point to obtain many ceramic materials and the microwave heating an appropiate preparative route for their sintering or boundary joining, particularly in those cases where at least one component shows an efficient microwave energy absorption [1–4]. The microwave heating takes place via dielectric losses, through a complex process in which the electromagnetic fields of the incident radiation induce motions of electrons and ions and rotate charge systems such as dipoles. The resistance to these induced motions results in an internal volumetric heating, with a reversal thermal gradient and flow of heat compared to conventional heating methods (convection and conduction) [5, 6]. This opens the possibility of a rapid and selective heating of a component in a given mixture of phases [7, 8]. These and many other applications of the microwave heating for the preparation of metal oxides-based materials are supported in a knowledge of the microwave irradiation effects on the properties of single metal oxides. In a study in this sense we have noted that under microwave irradiation many metal oxides behave as already established, however, in some cases different or not reported results were found, which are discussed in this contribution.

A total of 38 metal oxides were studied. Their selection was based in the following criteria: (a) be representaive of the different groups in the Periodic Table; (b) not previously studied from this point of view; (c) previously studied but with a reported behavior which needs to be reconsidered or confirmed. Under these criteria the following compounds were studied: MgO, CaO, SrO, BaO; TiO_2-Brookite, TiO_2-Anatase, TiO_2-Rutile; V_2O_5, MnO_2, α-Fe_2O_3, Fe_3O_4, CoO, Co_3O_4, NiO, CuO, ZnO, Ag_2O, ZrO_2, MoO_3, WO_3, CdO, α-Fe_2O_3, Ga_2O_3, In_2O_3, SiO_2, SnO, SnO_2, α-PbO_2, β-PbO_2, Sc_2O_3, Y_2O_3, La_2O_3, Nd_2O_3, Eu_2O_3, CeO_2, PrO_2, Pr_6O_{11} and Tb_4O_7. In order to minimize the role of impurities in their behavior all of them were analytical grade reagents (Johnson Mathey, BDH, Merck, Fluka, Aldrich). The irradiated samples weighed from 1 to 5 g. A commercial domestic microwave oven (from Sony) operating at 2450 MHz and at a power of 500 Watts was used. In all the cases the treatments were carried out in an air atmosphere. Irradiation times from 30 s to 20 min were used. The sample temperature during its microwave irradiation was estimated with an optical pyrometer [9]. Alumina crucibles were used as sample holders. All the samples were characterized, before and after their microwave treatment, by X-ray diffraction (XRD) using monochromatic CuK_α radiation and a HZG4 diffractometer (from Jena). Also ^{57}Fe and ^{119}Sn transmission Mössbauer spectra at room temperature were recorded when in the sample Fe or Sn was present. Mössbauer spectra were fitted using a least-square minimization algorithm and Lorentzian lineshape.

Behavior of oxides of non-transition metals. Oxides of non-transition metals generally show a poor coupling to microwaves, they are practically transparent to microwaves. We have observed that, with some exceptions, their temperature (estimated on the sample surface), for an irradiation time of 5 min, does not exceed 200 °C, too low to induce phase transitions or oxidation-reduction (redox) reactions in these compounds. These oxides usually are isolators and the oscillating electric field results insufficient to induce charge movements to allow their heating through the loss tangents mechanism in the microwave region. Exceptions are PbO_2 (α and β phases) and SnO, which are semiconductors

For PbO_2, Baghurst *et al.* [10] have reported a decomposition reaction on microwave heating to give Pb_3O_4 (without specify if the irradiated material was α-PbO_2 or β-PbO_2). In a more recent study, Gasgnier *et al.* [11] reported the reduction of Pb_3O_4 (minium phase) to three phases: PbO (massicot), PbO (litharge) and an unknown phase. We have irradiated α-PbO_2 or β-PbO_2 up to 20 min observing their reduction to Pb_3O_4 and finally to PbO (massicot and littharge) (see Fig. 1). The overal reduction reaction can be written as: $PbO_2 \rightarrow Pb_3O_4 \rightarrow$ PbO.

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