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 line-shape.

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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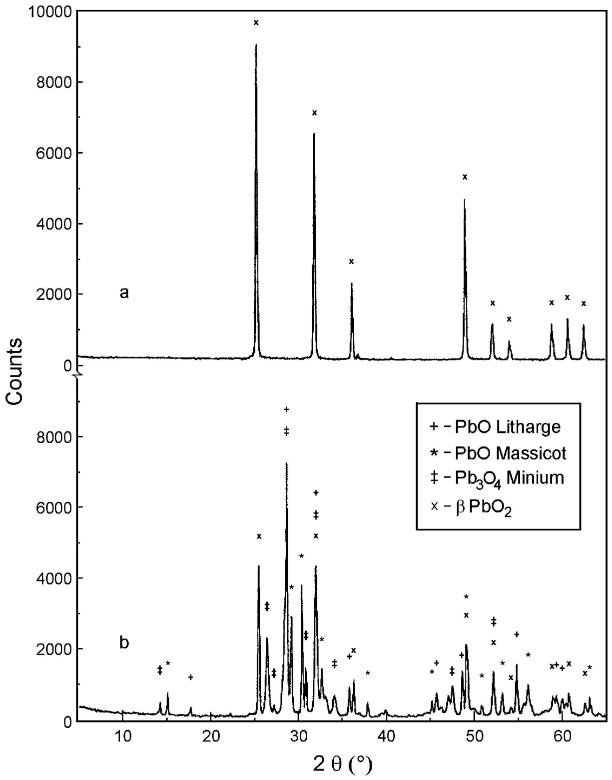
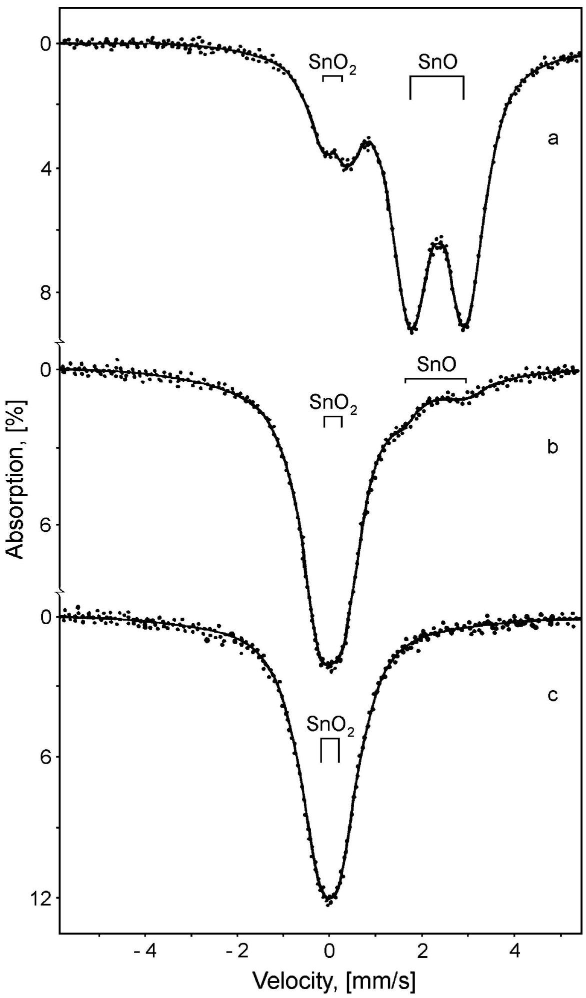


Figure 1 X-ray diffraction powder patterns of β-PbO_2 before (a) and after its irradiation with microwaves during 5 min (b). On microwave heating PbO_2 transforms into Pb_3O_4 and PbO.



Figire 2 ^{119}Sn Mössbauer spectra at room temperature of tetragonal (*black*) SnO with SnO_2 as impurity (a). Under irradiation with microwaves black SnO transforms into SnO_2 (b). After 4 min of irradiation the transformation is complete (c). No intermediate mixed valence compounds (Sn_2O_3 or Sn_3O_4) were found in the oxidation process from SnO to SnO_2.

SnO is one of the studied oxides that we found that easily coupled to microwaves at room temperature. However, in a previous study it was reported as a bad absorber [10]. We observed that SnO turns incandescent red after two min of irradiation, and then continues absorbing microwave energy. When the experiment ends in the sample only SnO_2 was identified, according to XRD.^{119}Sn Mössbauer spectra recorded at different irradiation times (see Fig. 2) suggest that in the first part of the experiment the oxidation of SnO to SnO_2 takes place, and then this end product continues absorbing microwave energy through a typical runaway process. Mössbauer spectrum of SnO is a well resolved doublet with $\delta = 2.71$ mm/s (relative to SnO_2) and $\Delta = 1.54$ mm/s while for SnO_2 it is an unresolved doublet with $\Delta = 0.45$ mm/s. SnO_2 is a bad microwave absorber at room temperature and only above 400 °C it efficiently couples to the incident radiation. XRD and^{119}Sn Mössbauer spectra do not support, in our conditions, the formation of a mixed Sn^{2+} and Sn^{4+} oxides, e.g. Sn_2O_3, and Sn_3O_4 which have been reported as intermediate products in the oxidation process of SnO [12].

Behavior of oxides of transition metals. In accordance with other authors [4, 7, 8, 10, 11, 13], we have observed that several transition metal oxides are good absobers of microwaves at room temperature. Particularly, MnO_2, Fe_3O_4, CoO, Co_3O_4, NiO, CuO, and Ag_2O turn incandescent red within the first minute of irradiation; WO_3, V_2O_5, Pr_6O_{11} and Tb_4O_7 also show a good coupling to microwaves but usually they require higher irradiation times to turn orange or red. All these oxides are semiconductor. In the following we will discuss in detail those cases where the heating process induce a structural transformation or a redox reaction.

MnO_2: On microwave heating this oxide reduces to β-Mn_2O_3 and γ-Mn_3O_4, being the last one the main product of the reaction, confirming already reported results [13].

Fe_3O_4: This compound strongly couples to microwaves, turning incandescent red during the first seconds and producing a characteristic bursting noise. The interaction of this material with microwaves has been well studied [8, 14]. This iron oxide is ferromagnetic and probably the magnetic losses are responsible for triggering the thermal runaway at room temperature. In Fe_3O_4 and binary ferrites, such as $BaFe_{12}O_{19}$ both, E and H fields of the incident electromagnetic wave participate of a strong interaction with the irradiated material allowing its rapid heating [6] and inducing pronounced structural transformations [14]. Above 588 °C (the Curie temperature of Fe_3O_4), the rate of heating begins to decrease, and at approximately 600 °C its oxidation to α-Fe_2O_3 (hematite) takes place, as reveal the XRD powder patterns and Mössbauer spectra of microwave-heated Fe_3O_4 samples (see Fig. 3). Futher heating must be due to dielectric losses but without

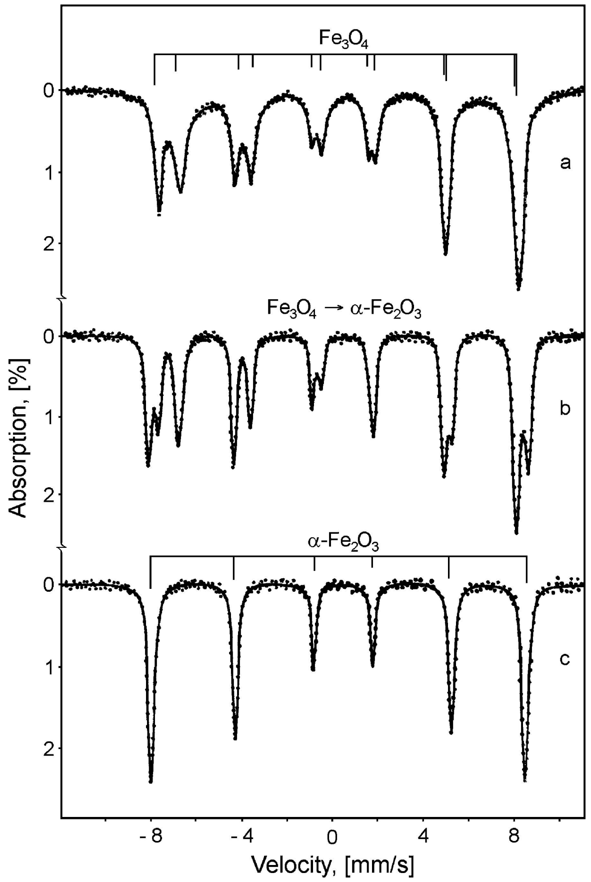


Figure 3 ^{57}Fe Mössbauer spectra at room temperature of Fe_3O_4 (a). Under irradiation with microwaves this iron oxide oxidizes and transforms into α-Fe_2O_3 (b). After two minutes of irradiation the transformation is complete (c) but without presence of other structures.

any structural transformation or redox reaction. The end product, α-Fe_2O_3 is a poor microwaves absorber and a stable iron oxide on heating in air. Other authors based in transmission electrons microscopy (TEM) results have reported the existence of various unknown structures in the reaction products, one of them probably α-FeOOH [10, 12]. However, we think that the occurrence of this iron oxyhidroxide is not possible since on microwave irradiation Fe_3O_4 reaches temperatures which exceed the stability range of α-FeOOH. On heating above 300 °C this iron oxyhidroxide transforms into α-Fe_2O_3 [15]. Our XRD powder patterns and Mössbauer spectra only reveal the existence of partially oxidized magnetite and α-Fe_2O_3 as the intermediate and end reaction products, respectively (Fig. 3) without presence of other structures.

Co_3O_4: The coupling of this compound to microwaves is similar to that above discussed for Fe_3O_4, probably prevailing the same physical interactions between the material and the electric and magnetic field of the incident electromagnetic wave, but in this case the end product is CoO.

CuO: This is one of the metal oxides that best couples to microwaves and was one of the first solid compounds with available dielectric data even at high temperature [16]. When CuO is irradiated with microwaves its temperature rapidly rises and in seconds becomes incandescent red and reduces to Cu_2O. The reduction process can be monitored through XRD and also using

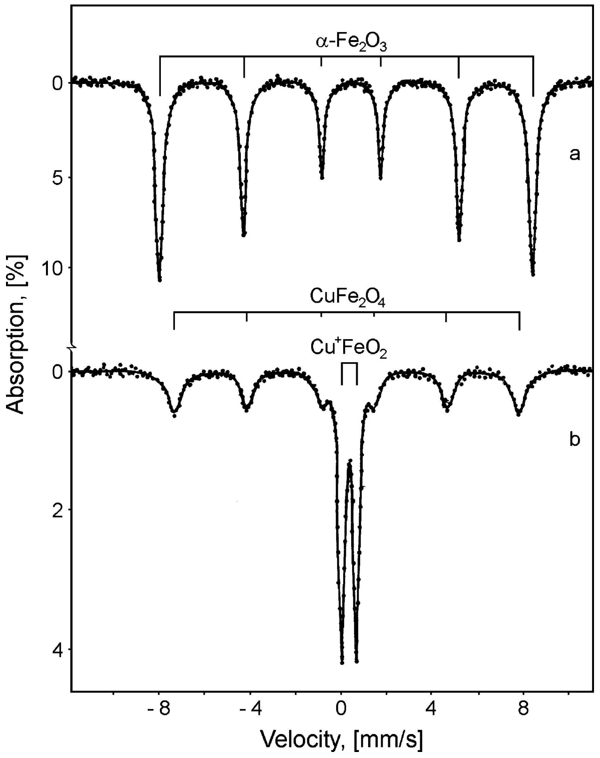


Figure 4 ^{57}Fe Mössbauer spectra at room temperature of a mixture of (CuO + α-Fe_2O_3) before (a) and after its irradiation with microwaves during 5 min (b). The central doublet corresponds to $CuFeO_2$ where according to the δ value (0.33 mm/s relative to α-Fe) iron appears as Fe^{3+} while copper remains in its monovalent state (Cu^+). On heating, from the mixture of oxides also cubic and tetragonal copper ferrites, $CuFe_2O_4$, are formed.

Mössbauer spectroscopy if a small amount of α-Fe_2O_3 is added to the sample to be irradiated. In this case, the formation of $CuFeO_2$ and a minor fraction of $CuFe_2O_4$, both cubic and tetragonal phases (a sextext of broad lines), are detected in the irradiated sample (see Fig. 4). According to the isomer shift value (0.33 mm/s relative to α-Fe) of the central paramagnetic doublet ($\Delta = 0.65$ mm/s), in $CuFeO_2$ iron is present in ferric state, Fe(3+), while copper appears as monovalent ($Cu^+Fe^{3+}O^{2-}{}_2$). No reflections due to Cu metal were observed in the XRD patterns of our CuO irradiated samples, which has been reported by other authors [10]. The presence of metallic Cu has also been reported when CuO is added to coal as microwave energy receptor during the coal pyrolysis [17], which is an expected result because the coal pyrolysis leads to reducing conditions. The reduction of CuO to Cu metal in air does not have parallel in conventional heating, except in presence of a reducing agent. The formation of Cu metal under microwave irradiation, as it has been reported [11], could be explained as resulting from a reducing effect of hydrogen radicals generated by decomposition of trapped water molecules. CuO is a material that has been widely used in the study of sintering process of ceramic materials using microwave heating. Perhaps the best known example in this sense is that related to the synthesis of high Tc superconducting ceramics [18] but without reports on Cu metal formation.

CoO and NiO: These two oxides are good microwave absorbers and within the first minute of irradiation become incandescent red; however, no differences were observed between XRD powder patterns recorded before and after different irradiation times indicating that they remain stable.

Ag_2O: This oxide has a semi-metal behavior which leads to its easy microwave heating with formation of metallic silver as end product.

V_2O_5 and WO_3: These two oxides have been reported as good microwave absorbers and this feature has been used in the synthesis of some ceramic materials, e.g. $BaWO_4$ from BaO and WO_3; and KVO_3 from V_2O_5 and KCO_3 [10]. No structural or redox reaction were detected in our XRD patterns of V_2O_5 and WO_3 samples even after 20 min of irradiation. The microwave heating of V_2O_3 has been studied in an oxidizing atmosphere leading to V_2O_5 formation [11], which, as expected, appears as the most stable phase in these conditions. V_2O_5 and WO_3 have been used as microwave energy receptors during the coal pyrolysis [17] obtaining some evidence on V(5+) reduction to V(4+) but not for W(4+).

Oxides of inner transition metals: Of the studied compositions within this family of oxides only Pr_6O_{11} and Tb_4O_7 were found good absorbers of energy from the incident microwave radiation. XRD powder patterns of the irradiated samples revealed the occurrence of pronounced structural transformations related to redox reactions. However, our results only confirm those already reported by Gasgnier *et al.* [13], no evidence of different or new structural changes was found.

Another group of transition metal oxides become good microwave absorbers only when they are irradiated from certain high temperature, known as critical temperature to be able the runaway process [4]. Among these oxides are TiO_2 (Brookite) and TiO_2 (Anatase) which when heated in a crucible immersed in MnO_2 in minutes transformed into TiO_2 (Rutile), the most stable phase of TiO_2.

In summary, our results on the effect of microwave irradiation on single metal oxides agree, for many of the studied compositions, with those already reported by other authors; however, for PbO_2 (α and β phases), SnO, Fe_3O_4, CuO and Ag_2O differences were found. The observed changes are similar to those expected from conventional heating. The microwave irradiation of these semiconductor metal oxides lead to their rapid heating but without modify the physical nature of the processes involved in their structural transformations and redox reactions on heating.

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