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LETTER

Solid state mixed oxides synthesis under microwave heating (JMSL10627-04)

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During the last 10 years the use of microwaves in chemistry has found many applications. This comes from the possibility of obtaining particular operative conditions not available through traditional synthetic methodologies. This is in fact an alternative heating tool for solid state synthesis is promising due to the increase of synthesis rate, the reduction of grinding steps during the synthesis process and for the peculiar property of the microwaves to heat a system ''from the inside'' [1]. Here we report on some microwave assisted solid state synthesis of inorganic solids of technological interest such as chromites, ferrites, spinels and garnets. The syntheses have been performed following conventional reaction scheme: oxide–oxide and oxide–decomposing intermediate. The oxide–metal in oxygen current and double salt thermal decomposition reactions have been reported already [2]. Domestic multimode microwave ovens (Whirlpool, Talent, 3D System 2.45 GHz) and alumina crucibles were used all over the experiments, grinding and/or mixing of reactants were performed, if necessary, by ball-milling in an agate jar (Retsch Mixer Mill). All reactants were Aldrich high purity compounds. In all the experiments, the amount of reacting mixture was approximately 5 g. The reacting powder was contained in alumina crucibles. Temperature was measured by optical pyrometry (IMPAC Infratherm, IGA8 plus). The maximum temperature reached during the reactions, measured by an optical pyrometer was 1160 K. For XRD analysis a Siemens D5000 instrument (Bragg-Brentano geometry, Cu Kα radiation) was used, the products were recognized using J.C.P.D.S. Powder Diffraction File (International Centre for Diffraction Data, Swarthmore, PA).

For the oxide–oxide reaction stoichiometric mixtures of the oxides for a total weight of 5.0 g was heated for 40 min at 700 W, for the synthesis of Pb_2CrO_5 the reaction time was only 3 min. Also when a precursor was used ($BaCO_3$ for barium stannate, Na_2O_2 for sodium tungstate and Na_2CO_3 for sodium aluminate) the reactants were in stoichiometric ratio.

All the above mixed oxides have been chosen as examples of technological materials because of their practical uses, e.g. electrical, optical, catalytic or chemical sensing properties. Lead basic chromate (chrome red) has been used as a ceramic pigment and can be prepared heating at 1120 K a mixture of PbO_2 and Cr_2O_3 in an electric furnace for some 10 min. The powder XRD spectrum of the product obtained by microwave heating is reported in Fig. 1.

Sodium tungstate is used as flame retardant of fabrics and as a mordant in dyeing. WO_3 is a good absorber for microwave [1] hence susceptor is not necessary. Na_2O_2 was used instead of NaOH because its decomposition at relatively low temperature (730 K) leads to freshly prepared Na_2O particles, which rapidly react with WO_3. The XRD spectrum is reported in Fig. 2. Yttrium vanadate, doped with Nd^{3+} or Eu^{3+} is used as solid state laser material and for phosphors production, respectively [3] and is normally prepared by hydrothermal method [4]. The rapid microwave assisted preparation yields a XRD pure product Fig. 3.

Yttrium iron garnet ($Y_3Fe_5O_{12}$), which is an interesting magnetic material, like many rare earth garnets

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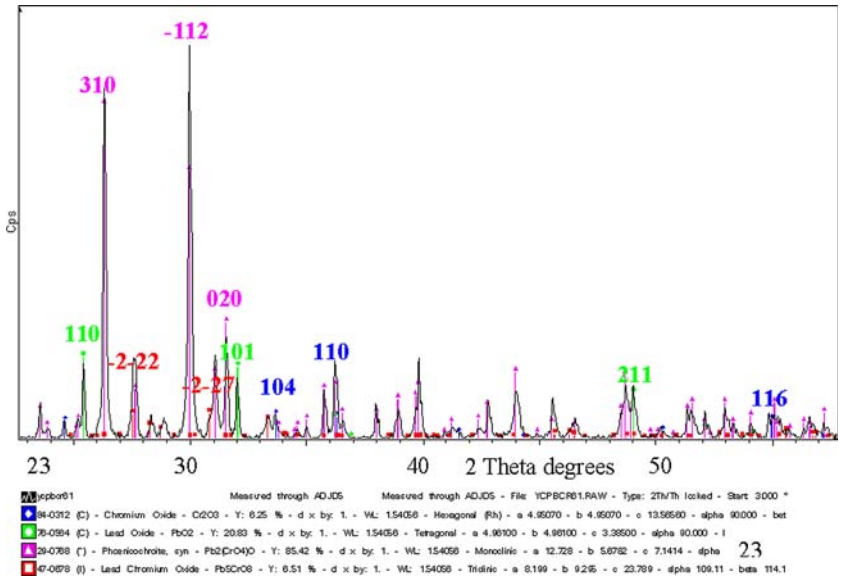

Fig. 1 $PbCr_2O_5$, XRD

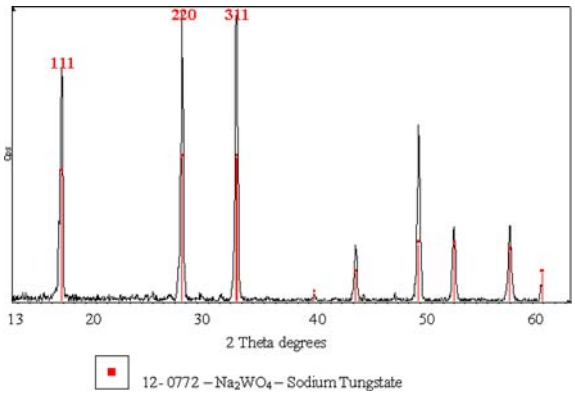

Fig. 2 Sodium tungstate, XRD

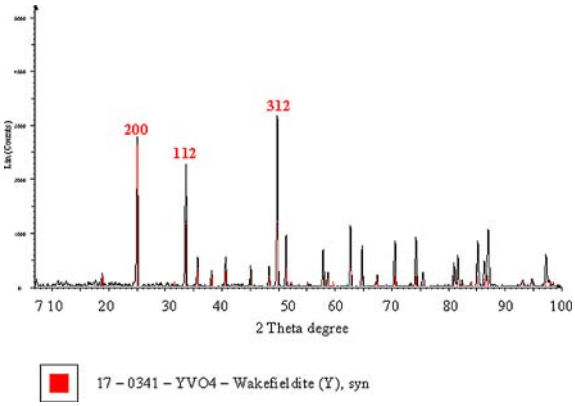

Fig. 3 Yttrium vanadate, XRD

[5], can be synthesised from the mixture of the oxides at 1670 K [6] or from the mixture of the hydroxides obtained from a solution of nitrates and chlorides followed by their calcination at 1170 K for 18–24 h [7]. The microwave method allows the preparation of the compound in a pure form; the XRD spectrum is reported in Fig. 4.

All the reactants but WO_3 are poor microwaves absorbers. To bring the reaction mixture to a temperature high enough to start the reaction the crucibles containing the reactants were surrounded by silicon carbide, which is a good microwave absorber [8]. Microwave heating has been demonstrated to be a very promising non-conventional tool for the solid state laboratory synthesis of many compounds. The rapid microwave heating leads to shorter reaction time. Microwave heating is ''from the inside'' of the sample and, in high temperature solid state chemistry, implies a sharp reduction of contamination from the crucible

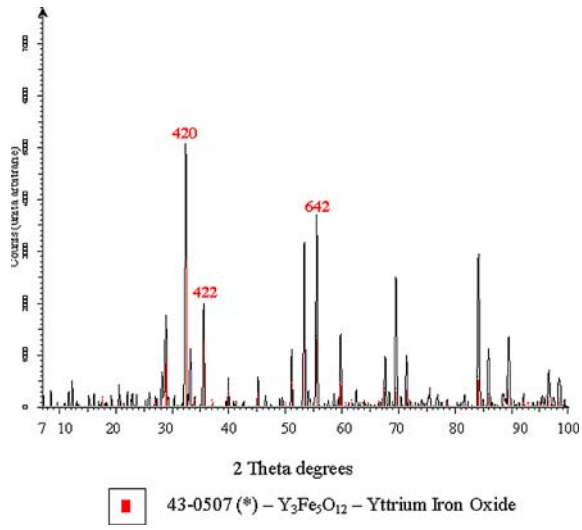

Fig. 4 Yttrium iron garnet, XRD

walls. The rapid power-temperature response leads to cost reduction, because there is no need to heat the entire refractory material which is part of a conventional oven. In some cases better yields have been also observed. Unfortunately the careful measurement of high temperature under microwave is still an unresolved problem as well as the influence of microwave on the reaction mechanism.

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