Application of Microwave Heating Techniques for the Synthesis of Solid State Inorganic Compounds

David R. Baghurst and D. Michael P. Mingos*

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, U.K.

A commercially available microwave oven operating at 2450 MHz and power levels of 50—500 W has been used to synthesise some ternary inorganic oxides in high yield, and in a fraction of the time required for conventional conduction heating methods.

During the last two years several publications have appeared which have indicated that it is possible to use commercially available microwave ovens for accelerating the rates of chemical processes in solution. Interesting applications have included the acceleration of nucleophilic substitution reactions of organic compounds,[1] the dissolution of geological samples in mineral acids,[2] and the preparation of short lived radiopharmaceuticals.[3] These applications have generally required Teflon containers which can accommodate the high pressures generated under these closed conditions. In this paper we report a novel application of microwave heating for the synthesis of solid state compounds in a fraction of the time required for conventional synthetic methods.

It has generally been assumed that inorganic oxides do not absorb microwaves strongly. Indeed many of the implements and containers associated with domestic microwave ovens are ceramic based. Our studies on inorganic oxides using a microwave oven operating at 2450 MHz and power levels of 50—500 W have established that although CaO, TiO_2, CeO_2, SnO, Al_2O_3, Pb_3O_4, Fe_2O_3, Cr_2O_3, and La_2O_3 do not absorb this microwave frequency strongly there are a substantial number of oxides which do. These oxides include ZnO, V_2O_5, CuO, MnO_2, PbO_2, and WO_3. This strong absorption is reflected in dramatic heating effects. 1—5 g Samples of V_2O_5 and WO_3 achieve temperatures in excess of 700 °C and melt within one min at the 500 W power level. The same quantities

of CuO achieve temperatures in excess of 550 °C at the same power level and for the same period of time. 5—10 g Samples of ZnO and MnO_2 reach temperatures in excess of 800 °C under the same conditions (the temperatures were measured using a Chromel/Alumel thermocouple between microwave exposures).

These properties have been used to develop convenient and high yield syntheses of solid state inorganic oxides. Each reaction was carried out in an alumina crucible resting on a firebrick in the microwave cavity. The products were characterised using powder *X*-ray diffraction techniques. Two types of reaction were studied: thermal decomposition and the syntheses of ternary oxides.

Simple thermal decomposition reactions are illustrated by the decomposition of PbO_2 to Pb_3O_4 where the reaction temperature reached a maximum of *ca.* 200 °C after 7 min and decomposition proceeded. Interestingly the temperature fell soon after this even though the sample continued to be exposed to microwaves. This is attributed to the fact that the product does not absorb microwaves strongly. Good yields of product (>80%) were obtained after total reaction times of 20—30 min and no metallic lead was formed in the reaction, in contrast to some literature reports.[4] The lattice parameters obtained for tetragonal Pb_3O_4 from *X*-ray powder diffraction were a = 8.806(1) and c = 6.558(2) Å which are in good agreement with the literature values, a = 8.815 and c = 6.565 Å.[5]

Combinations of compounds which do and do not absorb microwaves strongly have been heated in the microwave cavity resulting in the syntheses of ternary oxides. For example, CuO and Fe_2O_3 gave a mixture of the tetragonal and cubic phases of the cupro-spinel $CuFe_2O_4$ quantitatively. They were synthesised within 30 min using 500 W power levels. Conventional synthetic methods require 23 h. The product obtained by the microwave route contained more of the high temperature cubic phase which is thought to become more stable around 700—800 °C.[6] The lattice parameters obtained for the cubic form of $CuFe_2O_4$ were a = 8.395(2) Å (lit.[7] a = 8.38(3) Å). $BaWO_4$ was synthesised from BaO and WO_3 in 30 min in a quantitative manner, and this synthesis can be compared with conventional methods based on a precipitation reaction between $BaCl_2$ and Na_2WO_4 followed by annealing for 2 h at 800 °C. The measured lattice parameters for the tetragonal phase of $BaWO_4$ were a = 5.610(2) and c = 12.695(4) Å (lit.[8] a = 5.6134 and c = 12.720 Å). Similarly KVO_3 was produced quantitatively after 7 min from K_2CO_3 and V_2O_5 whereas the conventional synthetic routes require more than 12 h heating and several grindings and refirings to obtain a single phase.[9] The lattice parameters obtained for the orthorhombic phase of KVO_3 were a = 5.695(3), b = 10.800(7) and c = 5.181(3) Å (lit.[9] a = 5.70, b = 10.82, and c = 5.22 Å).

These preliminary results clearly indicate that it is possible to perform solid state inorganic syntheses using microwave techniques. Subsequent research will focus on defining the differences between conductive and microwave heating and will explore its applications to other ternary systems.[10] It will be of interest to discover systems where the two methods give either different compounds or phases. The mechanism of microwave absorption in these systems also needs to be defined in a chemically helpful way. We are currently attempting to obtain microwave spectra of solid samples in an attempt to define the spectral characteristics of chemically related binary inorganic compounds. Currently we believe that the strong absorption of microwaves by these oxides is related to their non-stoicheiometry.

Dr. A. M. Chippindale is thanked for many helpful discussions.

Received, 19th February 1988; Com. 8/00674A

References

1 R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, and J. Rousell, *Tetrahedron Lett.*, 1986, **27**, 279.
2 L. B. Fischer, *Anal. Chem.*, 1986, **27**, 279.
3 D.-R. Hwang, S. M. Moeriein, L. Long, and M. J. Welsch, *J. Chem. Soc., Chem. Commun.*, 1987, 1799.
4 E. W. Abel, in 'Comprehensive Inorganic Chemistry,' eds. J. C. Bailar, Jr., H. J. Emeleus, R. S. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, U.K., 1973, Vol. 2, p. 120.
5 *N.B.S. Circular 539*, 1958, **8**, 32.
6 E. H. Nickel, *Can. Mineral.*, 1973, **11**, 1003.
7 E. Prince and R. G. Treuting, *Acta Crystallogr.*, 1956, **10**, 1025.
8 *N.B.S. Circular 539*, 1957, **7**, 9.
9 R. S. Feigelson, G. W. Martin, and B. C. Johnson, *J. Crystal Growth.*, 1972, **13**, 686.
10 D. R. Baghurst, A. M. Chippindale, and D. M. P. Mingos, *Nature*, 1988, **332**, 311, describes the application of these microwave techniques for the synthesis of high temperature superconducting ceramics.