Microwave-assisted Synthesis of Inorganic Materials

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The use of microwave radiation has become a widespread and convenient method for heating food and beverage in modern society due to the energy efficient and volumetric heated observed with microwave radiation. The use of microwave or dielectric heating in chemistry has been limited, however, with most applications occurring in organic chemistry.[1] The fast and volumetric heating of organic reactions has lead to extraordinary reaction rate enhancements.[1] More recently the use of microwave radiation for heating reactions in the laboratory has expanded to inorganic and materials chemistry.[2,3]

Microwaves are generated by a magnetron tube. Magnetrons were developed by Randall and Booth at the University of Birmingham during World War II.[3] These devices operate similar to a cathode ray tube, consisting of a heated cathode, a voltage biased anode, a magnetic field, and an antenna. (Fig. 1) Electrons are emitted from the cathode and move along a spiral path, induced by the magnetic field, to the anode. As the electrons spiral outward, they form space charge groups, and the anode shape forms the equivalent of a series of high-Q resonant inductive-capacitive circuits. The microwave frequency generated in the anode is picked up by the antenna and is transmitted into the microwave cavity.

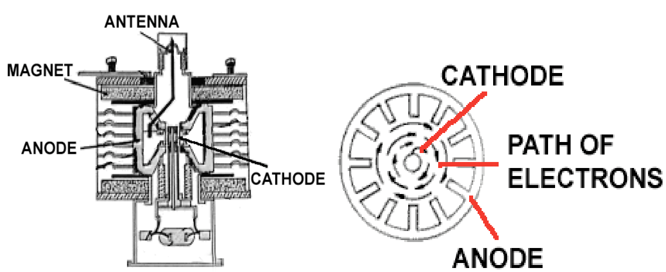

Figure 1: Simple diagrams illustrating the parts of a magnetron and the motion of electrons emitted from the cathode.[4]

There are several common misconceptions associated with microwave radiation. They are that microwave radiation is energetic enough to directly affect chemical reactions; heats matter by rotating molecules, and can cause non-thermal reaction rate enhancements. Looking at the energy of microwave radiation in Table 1, one can see microwaves lack the energy to affect any common chemical bond. The actual mechanism of microwave heating does involve molecular rotational energy induced by microwaves, but intermolecular collisions occur on the same time scale in liquid phases, approximately every 10^{-30} seconds. These collisions prevent any full molecular rotation, and the rotational energy induced by the microwave radiation is converted into vibrational and translational energy.[1] Other heating mechanisms, such as conductive and interfacial polarization, are present in solids under dielectric heating.[5] These are the primary mechanisms of heating with microwave radiation. Measuring the temperature of a reaction being heated with microwaves can be challenging, because the device used to measure the temperature can be affected by the radiation. All reaction rate enhancements have been shown to be thermally induced, in spite of claims to the contrary.[6]

	Microwave Radiation	Brownian Motion	Hydrogen Bonds	Covalent Bonds	Ionic Bonds
Energy (eV)	10^{-6} to 10^{-4}	0.026 (298 K)	0.04 to 0.44	4.51 (C-H) 3.83 (C-C)	7.6

Table 1: Energy associated with microwave radiation and different chemical bonds.[1]

One of the earliest applications of microwave radiation to the synthesis of inorganic compounds was performed by Frazer and Holzmann[7] followed quickly by Shriver and Jolly.[8] Frazer and Holzmann's work centered on the reductive dimerization of BCl_3 to B_2Cl_4, while Shriver and Jolly observed the transformation of $GeCl_4$ to Ge_2Cl_6 under microwave radiation. Continuing this early application of microwaves, Mingos and his co-workers expanded the application of microwave heating to solid state reactions. During their investigation it was observed that some metal oxides were sensitive to dielectric heating. Copper (I) oxide reached 550 °C after irradiation for 1 minute at 500 W. WO_3 and V_2O_5 heated to >700 °C under the same conditions, and melted upon further heating.[9] By applying these observations, Mingos and his co-workers were able to synthesize high-T_c superconducting oxides La_2CuO_4 and $YBa_2Cu_3O_{7-x}$.[10] This early work showed the utility of microwave radiation in the synthesis of inorganic compounds and materials due to the time and energy savings observed.

From these early applications microwave radiation has been applied to the synthesis of modern, advanced materials such as nano-materials[11], thin films[12], and porous ceramics.[13] There has been intense interest in the development of nano-materials because of their size dependent properties stemming from varying degrees of quantum confinement of the electrons in the material. El-Shall and his co-workers have developed a microwave-assisted synthesis for one dimensional cadmium and zinc chalcogenide rods and wires.[14] Their microwave process produced aligned, ultranarrow nanorods and nanowires. The fast and volumetric dielectric heating from microwaves made their synthesis very fast, and produced uniform materials.

The development of thin films is an important area of materials chemistry that has a large impact on the microelectronics industry. There are many methods for depositing thin films, and the morphology of the film is highly dependent on the method of deposition. In particular, Hui Yan and co-workers have shown that thin films of zinc and cadmium sulfide can be controllably deposited on glass substrates.[15] In addition, Richard Masel and co-workers have developed a novel method for the chemical vapor deposition of Ta_2O_5 utilizing microwave heating to produce the chemical vapor.[16] The microwave deposition of these films is advantageous because it does not require expensive high vacuum chambers, nor are these methods limited to slow depositions rates.

Finally, porous materials have become important in chemistry due to their catalytic and gas storage abilities. Historically, zeolites have found widespread usage,[17] but more recently metal-organic frameworks (MOFs) have come a useful analogue. A significant drawback to these materials is the energy and time intensive processes required for their synthesis. In the early 1990's for zeolites[18] and just recently for MOFs, microwave heating has been shown to dramatically increase the rate of formation of these materials.[19]

References

1. Loupy, A., Ed.; In *Microwaves in Organic Synthesis;* Wiley-VCH Verlag GmbH & Co: Weinheim, 2002. pp 1-73.
2. Clark, D. E.; Sutton, W. H. Microwave Processing of Materials. *Annu. Rev. Mater. Sci.* **1996**, *26*, 299-331.
3. Mingos, M. P.; Baghurst, D. R. Tilden Lecture: Applications of Microwave Dielectric Heating Effects to the Synthetic Problems in Chemistry. *Chem. Soc. Rev.* **1991**, *20*, 1-47.
4. Gallawa, J.C. In *THE COMPLETE MICROWAVE OVEN SERVICE*. Prentice Hall, 2000.
5. Gavin Whittaker, personal correspondence.
6. Galema, S. A. Microwave Chemistry. *Chem. Soc. Rev.* **1997**, *26*, 233-238.
7. Frazer, J. W.; Holzmann, R. T. "Microwave Excitation as a Synthetic Tool: The Preparation of Diboron Tetrachloride" *J. Am. Chem. Soc.* **1958**, *80*, 2907-2908.
8. Shriver, D.; Jolly, W. L. "The Microwave Synthesis of Digermanium Hexachloride" *J. Am. Chem. Soc.* **1958**, *80*, 6692-6693.
9. Baghurst, D. R.; Mingos, M. P. Application of Microwave Heating Techniques for the Synthesis of Solid State Inorganic Compounds. *J. Chem. Soc., Chem. Commun.* **1988**, *12*, 829-830.
10. Baghurst, D. R.; Chippindale, A. M.; Mingos, D. M. P. Microwave syntheses for superconducting ceramics. *Nature* **1988**, *332*, 311.
11. a) Cushing, B. L.; KolesnichenkoV. L.; O'Connor, C. J. Recent Advances in the Liquid-Phase Syntheses of Inorganic Nanoparticles. *Chem. Rev.* **2004**, *104*, 3893-3946. b) Mirkin, C.A. The Beginning of the Small Revolution. *Small* **2005**, *1,* 14-16.
12. a) Wilk G. D.; Wallace R.M.; Anthony J.M.; High-kappa gate dielectrics: Current status and materials properties considerations *J. App. Phys.* **2001**, *89*, 5243-5275.
13. a) Kacirek, H.; Lechert, H. Investigations on the Growth of the Zeolite Type NaY., J. Phys. Chem. **1975**, *79*, 1589-1593. b) Li H., Eddaoudi, M., O'Keeffe, M., Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, *402*, 276-279.
14. Panda, A. B.; Glaspell, G.; El-Shall, M. S. Microwave Synthesis of Highly Aligned Ultra Narrow Semiconductor Rods and Wires. *J. Am. Chem. Soc.* **2006**, *128*, 2790-2791.
15. Zhai, R.; Wang, S.; Xu, H.; Wang, H.; Yan, H. Rapid formation of CdS, ZnS thin films by microwave-assisted chemical bath deposition. *Mater. Lett.* **2005**, *59*, 1497-1501.
16. Ndiege, N.; Subramanian, V.; Shannon, M. A.; Masel, R. I. Rapid Synthesis of Dielectric Films by Mircowave-Assisted Atomspheric CVD. *J. Chem. Soc., Chem. Commun.* Submitted.
17. Virta, R. L. In *2005 Minerals Year Book: Zeolites*. USGS, Washington D. C. 2005.
18. a) Chu, P.; Dwyer, F. G.; Clarke, V. J. *Eur Pat* 358 827, 1990. b) Arafat, A.; Jansen, J.C.; Ebaid, A.R.; van Bekkum, H. Microwave preparation of zeolite Y and ZSM-5. *Zeolites* **1993**, *13*, 162-165
19. Ni, Z.; Masel, R. Rapid Production of Metal-Organic Frameworks via Microwave-Assisted Solvothermal Synthesis. *J. Am. Chem. Soc.* **2006**, *128*, 12394-12395.