

Microwave syntheses for superconducting ceramics

SIR—The extraordinary research efforts that have followed the discovery of the high-critical-temperature superconducting ceramics based on copper oxides^{1,2} have concentrated primarily on the unique physical properties of these materials, their structural characterization and the development of theoretical models³. The development of alternative procedures for synthesizing these compounds has received less attention.

Recently we have discovered that several inorganic oxides including CuO, absorb microwave radiation of 2,450 MHz, which is the frequency used in domestic microwave ovens, very strongly⁴. As a result of this strong absorption, 1–5-g samples of CuO achieve temperatures in excess of 550 °C after a 1-min exposure in a commercially available microwave oven operating at a power level of 500 W. We have used this oven to synthesize mixed metal oxides, including those with superconducting properties.

The procedures adopted and the times required for the experiments can be gauged by giving details of the specific synthesis of La₂CuO₄. La₂O₃ (12.28 g) was mixed with CuO (3.00 g) by mechanical shaking and intimately mixed using an agate mortar and pestle. The mixture was placed in an alumina crucible and supported on a firebrick in the oven. A minute after the oven was turned on the mixture was glowing orange; this glow was maintained for a further 9 min and the mixture became molten, whereupon the oven was switched off. The product was allowed to cool and then ground to a fine powder, which was shown to be mainly La₂CuO₄ by X-ray powder diffraction. To convert the mixture into pure La₂CuO₄ it was heated for a further 30 min using variable powers of 130–500 W and then cooled and ground. The refined cell constants of the La₂CuO₄ were: $a = 5.354(1)$ Å, $b = 5.402(1)$ Å and $c = 13.149(1)$ Å (ref. 5).

Conventional heating techniques would typically require 12–24 h for this synthesis, so synthesis in a microwave oven leads to the isolation of a pure product in a fraction of the time usually required for conductive heating methods. Furthermore, X-ray diffraction experiments indicate the final product is not only of high purity but also of high crystallinity.

La_{1.85}Sr_{0.15}CuO₄ was similarly synthesized using CuO, La₂O₃ and SrCO₃ in the appropriate stoichiometric ratios. The first microwave heating cycle was completed in 6 min, and further cycles of 23 and 5 min lead to a pure sample, as determined by X-ray diffraction experiments with a tetragonal cell of dimensions: $a = b = 3.7751(4)$ and $c = 13.224(3)$ Å (ref. 6).

YBa₂Cu₃O_{7-x} was synthesized from

CuO, Y₂O₃ and Ba(NO₃)₂ in the appropriate stoichiometric ratios. The mixture was heated in a modified microwave oven which enabled the liberated NO₂ gas to be safely expelled. When treated with microwave radiation at a power level of 500 W for 5 min all the NO₂ was liberated and a powder diffraction pattern showed that no Ba(NO₃)₂ remained in the sample. The mixture was reground and exposed to microwaves (130–500 W) for a further 15 min, reground and exposed for an additional 25 min. Powder diffraction studies showed that the major component of the mixture at this stage was YBa₂Cu₃O_{7-x}, but there were some lines of low intensity due to Y₂BaCuO₅ (ref. 7). An additional exposure to microwaves for 25 min resulted in an essentially pure sample, with a tetragonal unit cell of dimensions $a = b = 3.861(2)$, $c = 11.789(7)$ Å (ref. 7). The conversion of

this tetragonal form into the superconducting orthorhombic form is achieved by slow cooling in the conventional manner⁷.

Having established that microwave heating provides a convenient and rapid mode of synthesis for the new class of high-temperature ceramic superconducting materials, we are now investigating the physical properties of these materials to establish whether this unusual mode of synthesis leads to any unusual properties.

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Punctuation in perspective

SIR—The important issue raised by Eldredge and Gould¹ in response to my News and Views comment² on Sheldon's paper³ concerns the role of 'species selection'. I wrote "I do not think that the attempt to explain morphological evolution by species selection can survive . . . But there never was much sense in the idea anyway". In their reply, Eldredge and Gould agree that it makes no sense, but say that this characterization is entirely of my own making. Not so.

To show this, I must quote. Gould wrote⁴ "Speciation is not always an extension of gradual allelic substitution to greater effect, but may represent, as Goldschmidt argued, a different style of genetic change — rapid reorganisation of the genome, perhaps non-adaptive. Macroevolutionary trends do not arise from the gradual adaptive transformation of populations, but usually from a higher-order selection operating on groups of species, while the individual species themselves generally do not change". Expressing a similar idea, Stanley wrote⁵ "If rapidly divergent speciation interposes discontinuities between rather stable entities (lineages), and if there is a strong random element in the origin of these discontinuities (in speciation), then phylogenetic trends are essentially *decoupled* (his italics) from phyletic trends within lineages . . . Then what determines the course of most phylogenetic trends must be a selection process in which species are the units". These "trends" must be morphological, because morphology is all, or almost all, that we see in the fossil record. I am delighted that Eldredge and Gould have abandoned species selection as a significant cause of morphological evolution,

but they really must not pretend they never said otherwise.

I say that species selection is the important issue, because big claims have been made for punctuational theory. The article by Gould quoted above is entitled "Is a new and general theory of evolution emerging?" (the answer of course is yes), and the opening words are "The modern synthesis, as an exclusive proposition, has broken down". Such a claim cannot be justified by what Eldredge and Gould say in reply to my article. The insistence that allopatric speciation is "the very heart and soul of punctuated equilibria", or that the rates of evolution in lineages leading to new major taxa are orders of magnitude greater than those observed (for example) in trilobites, imply no break with the modern synthesis. The former concept was Mayr's⁶ central thesis, and the latter was Simpson's⁷: Mayr and Simpson, of course, were two of the major architects of the synthesis. The only new idea in the theory of punctuational equilibria that could, if correct, justify claims of a new evolutionary paradigm is the idea of species selection as outlined in the quotations above.

Two lesser points. Eldredge and Gould suggest that the changes described by Sheldon are too small to shed much light on the origin of taxa above the species level. This may, or may not, be true, but it is an odd claim for Eldredge, at least, to make. In his book⁸ explaining the theory of punctuated equilibria, the only example discussed at any length is his own study of changes in the number of lenses in the eyes of trilobites. Why a change from 18 to 17 columns of lenses in the eye is relevant, whereas a change from 11 to 13 pygidial ribs³ is not, defeats me. (It was, in fact, the close similarity between the traits