Ceramic combinatorial syntheses exploring the chemical diversity of metal oxides

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ABSTRACT

A ceramic combinatorial method to investigate the phase space of e.g. metal oxides by a single sample is reviewed along with its application to cuprate superconductors. The main idea behind this method is to use a large number N of starting materials (micrometer size grains) to generate local reaction centers producing possible compounds at the reaction temperature. Mathematical calculations using also empirical data on the occurrence of compounds in phase systems allow to conclude that in 1 cm^3 of a sample, there are enough grains to populate all local reaction centers in order to obtain in principle what the N starting materials can produce. A variety of characterization technics have been applied to such libraries to identify e.g. cuprate superconductors. Finally the success of the concept will depend on analytical tools allowing for a simultaneous analysis of the composition and physical properties. Here, we have applied for the first time scanning SQUID microscopy to reveal local superconductivity in inhomogeneous ceramic samples.

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1. Brief history

Exploration of materials synthesis performing reactions in *parallel* started by the work of J. J. Hanak, introduced as "multiple-sample concept" [1]. However, at the time computational support for the preparation of multicomponent samples, their analysis and administration was not sufficient [2,3]. So it was only later that people took advantage of this idea by preparation of libraries by applying different methods:

(i) X.-D. Xiang et al. presented a pixel approach through solutions of starting materials by depositing consecutive layers by the help of different masks [4].
(ii) H. Danielson et al. created more than 2500 compositions for libraries by applying evaporation of many components via physical vapor deposition (PVD) and a physical masking scheme [5].
(iii) J. Wang at al. have applied a 2D combinatorial method in combination with photolithography to generate variable grading composition [6].

Although combinatorial approaches were applied to many classes of materials, mainly in the field of heterogeneous catalysis

and luminescence new materials were found and further optimized by such techniques [7–10]. This is mainly due to the fact that the analysis of pixel based reaction plates can be used for an analysis of "hot spots" in parallel as well. In other fields such as oxide super-conductors, known compounds could be reproduced [4], but now new cuprates had emerged so far. Being aware of all these attempts, we were searching for a process that should produce most ther-modynamically accessible phases at conditions of composition, T and e.g. P(O$_2$).

At first, this was a purely mathematical issue related to effects of packing of initial grains and their local reaction behavior. Finally, calculation led to the so called "single sample concept" (for the theoretical model see Chapter 2).

In this work, a variety of characterization technics such as transition electron microscopy combined to energy dispersive X-ray spectroscopy (TEM-EDX), nonlinear optics (NLO), scanning py-roelectric microscopy (SPEM), scanning SQUID microscopy (SSM) and magneto-optics (MO) have been applied to the libraries to demonstrate the formation of compounds showing properties such as luminescence, optical nonlinearity, ferroelectricity and superconductivity.

However, combined techniques (composition, structure, prop-erties) are still missing by today. The most promising advanced technic for the detection of magnetic properties and composition would be SSM and TEM-EDX.

2. Single sample concept

Metal oxides represent a class of materials covering most physical solid state properties of interest. Efficient exploration of their chemical diversity is thus a main issue in developing new methods for syntheses. Here, we review progress in *ceramic combinatorial chemistry*, i.e. attempts to explore the phase space by a *single sample* made up by a mixture of a large number *N* of starting materials [11–14]. The idea behind this approach is to form local products within an assembly of reacting grains of a certain size. Basically we can distinguish between (I) reacting small (300–1000 nm) grains completely or (II) reacting large grains (100–500 μm) by necking. Starting materials may be primary ox-ides or any multi-component grains. In case (I) the stoichiometry of *local products* is driven by the total amount of starting materials present at a reacting center. For a system where grains do not completely disappear (II) intergrain zones (necks) are producing the phases which do exist according the phase diagram of all involved components at temperature T (and p(O$_2$)). These ap-proaches (I), (II) have been applied to the local formation of lumi-nescent [15], second harmonic generation [15], ferroelectric materials [16,17] and in particular to cuprate superconductors [18].

Because of a large amount of *intergrown product grains*, the procedure finally needs analytical tools which provide at once compositional analysis and property information. This is in particular challenging in the search for new superconductors. Because of the extreme diamagnetism of superconductors (about 10^3 larger than for normal state matter), *magnetic separation*, however, can be very effective in extracting these phases for external analyses [19–21].

3. Theoretical model for exploring the phase space

A most simple model to demonstrate the efficiency of a *single sample* approach will be restricted to conditions of thermodynamic equilibrium at reaction conditions T and p(O$_2$). Given the number *N* of primary starting oxides, the number of possible phase diagrams N_q^{PD} can be calculated from,

$$\binom{N}{q} = \frac{N!}{q!(N-q)!} \,, \tag{1}$$

i.e. the number of combinations without repetition. Here, *q* denotes the number of components for each diagram. Consequently, we can have systems with $q = 2, 3, 4,\dots$ metals. Here, we encounter an interesting basic question in solid state chemistry: Is there an upper limit to *q* for constitutional metallic components and what is the statistical answer from chemical and mineralogical data bases?

The present answer is this: Both for minerals and man-made oxide compounds it seems that $q = 6$ is a realistic upper limit. In view of property generation, less than 6 constitutional cations are, however, sufficient to generate known physical properties of oxide compounds.

Up to here we know only the number N_q^{PD} of phase diagrams. But, what may be the number of possibly existing phases?

The number of phases is,

$$N^P = \sum_{i=2}^{q} <\eta_i> N_i^{PD} \,, \tag{2}$$

where η_i is the average number of phases, i.e. stoichiometries per diagram of the order *q*. An estimate for η_i is obtained by searching known data on oxides [14]. From this we may assume the following values:

$$<\eta_2> \approx 2, \ <\eta_3> \approx 3, \ <\eta_4> \approx 2-3, \ <\eta_5> \approx \ <\eta_6> \approx 1.$$

In special case of Tl and Hg containing cuprates η_4 can reach 3 or 4. In order to populate all this phase diagrams and phases N^P therein, the sample must provide a number of *local configurations* N_n^c being much larger than the number of N^P including a surplus for varying the stoichiometry in case (I).

The number N_n^c of local configurations reads as

$$N_n^c = \binom{N+n-1}{n} - N, \tag{3}$$

where *n* is the number of grains belonging to a particular config-uration C (*q*,*n*), with $n \geq q$. (The second term in Eq. (3) accounts for those containing a single element.)

Estimating *n* (the number of grains in a configuration) needs empirical data on the packing density in powder assemblies or simulation results. A reasonable value for <*n*> is of the order of ~ 8. Consequently, with <*n*> > *q* > 6 all phase systems are in principle addressed. A final issue deals with the total number of grains in a single sample (pressed pellet) which are necessary to build up all C(*q*, *n*), (*q* = 2, ..., 6; *n* = 2, ..., 8, ...). Assuming an average size range <d> of ~1 μm, a sample of 1 cm^3 (several pellets reacted at the same conditions T, p(O$_2$)) contains roughly 10^{12} grains. In case of a bit larger particles, e.g. 10 μm, we would have 10^9. These amounts of particles are by far large enough to provide all required variation.

We are about to draw a far reaching chemical conclusion: *A system of N different starting materials reacted within a grain as-sembly of the micrometer size range is in principle able to produce all possible (constitutional) solid phases within less than one cm^3*.

Important to notice here, that we do not attempt the formation of a single phase. Thus, a composition within C (*q*,*n*) that does not represent a possible stoichiometry will nevertheless produce some products, provided the present amount is still within the compo-sitional range of the corresponding phase diagram (typically within the distance Δ*x* separating two eutectic points).

Let us now consider the example of cuprate superconductors in more detail: Known data on these materials show that N = 10