Analele Universităţii de Vest din Timişoara
Vol. XLVII, 2005
Seria Fizică

DoE AND OPTIMIZATION IN SOLVOTHERMAL SYNTHESIS OF TERNARY CHALCOGENIDE NANOCRYSTALS

Terezia Nyari

INCEMC—Condensed Matter Research Institute Timisoara, Str. Plautius Andronescu 1, 300224 Timisoara, Romania; E-mail: nyarit@icmct.uvt.ro

Abstract
In this paper a statistical design of experiments (DoE) for the systematization of the parameter fields and process optimization of the solvothermal synthesis of ternary chalcogenide nanocrystals is reported for the first time.
Keywords: design of experiments, solvothermal, ternary chalcogenide nanocrystals

1. Introduction

Solvothermal synthesis is one of the most powerful routes to nanomaterials with different morphologies [1, 2]. In solvothermal synthesis of ternary chalcogenide nanocrystals, there are a variety of physical and chemical parameters that can be chosen and combined: type and concentration of precursors, reaction temperature, reaction pressure, pH value of the systems, type and concentration of solvents, introduction and removal of templates and other additives, choice of different autoclave geometries etc. [3-5]. Different combinations of these parameters lead obviously to products with different physical and chemical properties. For a product with given properties to be obtained, the optimum solvothermal synthesis conditions for which the desirable product is thermodynamically stable must be established on the basis of stability diagrams [6]. However, such well established models for the synthesis and growth processes of ternary chalcogenide nanocrystals are lacking and usually the process variables are adjusted empirically in a trial-and-error manner. This needs very laborious experimental work. Statistical design of experiments (DoE) can help to minimize the number of such trial-end-error experimentations, saving time and costs. In this work, an attempt of factorial DoE based on Taguchi method for the systematization of the parameter fields and process optimization of the solvothermal synthesis of ternary chalcogenide nanocrystals is reported for the first time.

2. DoE with Taguchi method

Taguchi's method makes use of an experimental process for finding an optimal design [7]. The search objective is to maximize a design metric over the design space, where each evaluation in the design space incorporates the noise space variations. Hence, for each experimental point in the design space (called "inner array" by Taguchi), the design metric (called the "S/N ratio" by Taguchi), as a function of the experimental arrangement of the $PPs\vec{x}_j$, is

$$S/N(\vec{x}_j) \equiv -10\log\left[\sum_{i=1}^{m}(PP(\vec{x}_j,\vec{p}_i)-\tau)^2 \times 1/m\right] \tag{1}$$

where *PP* is the one performance parameter being considered, *m* is the number of noise parameter arrangements $p_i^{'}$ and τ is the desired target value [8].

The points in the noise space $\vec{p}_i$ (called "outer array" by Taguchi) are chosen using a factorial method (called "orthogonal arrays" by Taguchi). Fractional factorial designs [7] are used to reduce computation. Taguchi provides justification for using his design metric based on the first two terms of a Taylor series expansion of societal loss [7]. It is assumed in this derivation that the preliminary design has been completed, and the optimal values of the design parameters need to be determined. The search over the design space is intended to maximize the metric of Eq. (1) above. The issue of how to search across the design space is an entirely separate issue from how to model the noise space variations. In Taguchi's method, the search across the design space is performed in precisely the same fashion as the approximation of the noise space is performed: using a factorial method. That is, the arrangement of design parameters with the highest *S/N* ratio is chosen. Of course, another round of experiments can be performed around that optimal point for a finer resolution, provided that certain conditions are met.

For the implementation of a Taguchi DoE, the following steps are needed [7]:

1. Problem Definition
2. Identify Ideal Function
3. Identify Control Parameters
4. Identify Noise Parameters
5. Conduct Experiments & Analyze Data
6. Select Best/Optimum Parameter Values
7. Confirm Results

3. Example of Taguchi DoE for solvothermal synthesis of chalcogenide nanocrystals

The desired parameters of the I-III-VI_2 (I = Cu; III = In, Ga; VI = S) nanocrystals to be obtained are:

1. stoechiometry variation: max. 5%;
2. single phase product;
3. controlled morphology in the 5-100 nm range (nanoparticles, nanorods);
4. low dimensional dispersion.

These four objectives can be translated into two criteria to be optimized simultaneously:

1. $CuInS_2$ ($CuGaS_2$) content of the product – to maximize

(measuring methods: XRD phase analysis, elemental analysis)

2. R = A_{max}/A_{min} (A = particle axis)

- for particles – target (R=1);
- for elongated morphologies – to maximize;

(measuring methods: TEM image analysis – ScionImage software).

For the optimization of the above criteria, three separate experiment plans has been made corresponding to three different solvents to be used: water (hydrothermal), ethylenediamine (aminothermal) and etylene glycol (glycothermal). The selection of control parameters has been made on the basis of preliminary experimental results. Thus, in the case of hydrothermal synthesis for instance, the chosen control parameters with two value levels are presented in table 1.

Table 1 Control parameters and values

Control parameter	Symbol	Values	Level
Precursors	A	CuCl, InCl3, thiourea	1
		CuCl, GaCl3, thiourea	2
Concentration	B	0,05 M	1
		0,2 M	2
Surfactant	C	Yes	1
		No	2
Temperature	D	120 ^{o}C	1
		180 ^{o}C	2
Time	E	5 h	1
		15 h	2
Filling rate	F	70%	1
		90%	2
Ultrasonic treatment	G	Yes	1
		No	2
TOTAL	**7 control parameters with 2 levels**		

The suitable orthogonal arrays for the experiments were selected for the case of each solvent using Qualitek 4 software application. For instance, in the case of hydrothermal synthesis (7 control parameters with 2 levels) an L8 fractional factorial array was chosen and the following test matrix resulted (table 2):

Table 2 Test matrix for hydrothermal synthesis

Test no.		Control parameters							Effects	
		A	B	C	D	E	F	G	%CIS (CGS)	R_{mean}
1		1	1	1	1	1	1	1	*	*
2		1	1	1	2	2	2	2	*	*
3		1	2	2	1	1	2	2	*	*
4		1	2	2	2	2	1	1	*	*
5		2	1	2	1	2	1	2	*	*
6		2	1	2	2	1	2	1	*	*
7		2	2	1	1	2	2	1	*	*
8		2	2	1	2	1	1	2	*	*

Note that the « * » values are the means of at least 3 measured values for each test (synthesis experiment).

One can see that this experiment plan requires only 8 tests to be done. Comparatively, a full factorial one would necessitate, for the same 7 control parameters with 2 levels, a number of $2^7 = 128$ synthesis experiments! Nevertheless, the information provided by a fractional factorial plan of experiments is somewhat poorer and is recommended for decision making in early stages of the research. For a deeper understanding of the underlying phenomena, especially in the case of interactions between control parameters, more refined DoE must be done.

After the test synthesis experiments has been done and the effect's measured values introduced in table 2, the data has been analyzed (Main effect, ANOVA, S/N, possible interactions between control parameters) using Qualitek 4 software and the optimum levels of control parameters with respect to evaluation criteria has been determined.

Based on these DoEs, significant improvements in the controlled solvothermal synthesis of I-III-VI_2 nanocrystals has been achieved by a well reduced number of experiments in our research projects [9, 10].

4. Conclusions

In summary, a statistical design of experiments (DoE) based on Taguchi method has been applied for the first time aiming to optimize the process of the solvothermal synthesis of ternary chalcogenide nanocrystals. Significant improvements of I-III-VI_2 nanocrystals quality has been achieved by a reduced number of experiments. The method established here may be applied for the DoE of other solvothermal experiments in the future.

Acknowledgements

Financial support from MATNANTECH and COPBIL research programs of the Romanian Ministry of Education and Research is gratefully acknowledged.

References

[1] Patzke G. R., Krumeich F., Nesper R., Angew. Chem. Int. Ed. **41** (2002) 2446

[2] Byrappa K., Yoshimura M., *Handbook of Hydrothermal Technology*, Noyes, Park Ridge, N.J., 2001

[3] T. Nyari, P. Barvinschi, R. Baies, P. Vlazan, F. Barvinschi, I. Dékány, Journal of Crystal Growth, 275 (1-2), e2383-e2387 (2005)

[4] T. Nyari, P. Barvinschi, P. Vlazan, O. Sandru, I. Dékány, Proceedings 27th International Semiconductor Conference (IEEE Catalog Number 04TH8748; ISBN 0-7803-8499-7), 445-448 (2004)

[5] T. Nyari, P. Vlazan, Sz. Papp, P. Barvinschi, I. Dékány, Analele Universitatii de Vest din Timisoara - Seria Fizică, 45, (2004) 267-270

[6] Lencka M. M., Riman R. E., Chem. Mater., 5 (1993) 61

[7] Alexis J., *Metoda Taguchi. Planuri de experiențe*, Ed. Tehnică, Bucureşti (1999)

[8] Byrne D. M., Taguchi S., *The Taguchi approach to parameter design*, in Quality Congress Transaction – Anaheim, pages 168–177. ASQC, May 1986

[9] PNCDI-MATNANTECH, Contract MEC-INCEMC No. 136(305)/2003

[10] Bilateral Romania-Hungary Project INCEMC-University of Szeged (RO-5/02)