Optimization of Doping Process Parameters of Cerium Vanadate Doped with Be, Mg, Ca, Sr, and Ba Ions

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Abstract: In this research, Taguchi method was applied to determine optimum parameters of doping process of cerium vanadate with Be, Mg, Ca, Sr, and Ba ions. Percentage and type of doping ions are used as parameters in optimization process applied as orthogonal array to decrease the number of experiments. The calculated unit cell volume by Rietveld Refinement analysis via X-ray diffraction data (XRD) were used to confirm the formation of doped cerium vanadates. ANOVA method was applied to determine the effectiveness of the parameters.

Keywords: Cerium vanadate; metal doping; X-ray diffraction; Rietveld refinement method; Taguchi optimization method.

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INTRODUCTION

The fundamental key of the industry's success is product quality concerning of the customers and manufacturers with consistency and production rate (1). There are many factors contributing to production which is directly related to quality. In 1920s, Fisher (2) determined the optimum treatments in order to produce the best conditions called Design of Experiments (DOE) as a statistical approach to investigation of a system or process. DOE as a statistical approach give only the relationship between input and output data. On the other hand, a fractional factorial design can be described by selecting a limited number of experiments including the most informative possibilities in order to reduce costly and time-consuming experimental procedure (3, 4). The complexity and non-clear guideline of this optimization method caused to form innovative approaches. Dr. Genichi Taguchi (1) developed an optimization method entitled Taguchi Method to consider these difficulties of the previous methods (5, 6). In the last two decades, Taguchi Method has drawn much more attention in many applications such as process optimization (7, 8), component design (9), and manufacturing system (10) due to its practical application for determining optimum parameters for high quality systems.

The third period of transition metals in the periodic table is called lanthanides or rare earths which contain fifteen different elements such as La, Ce, Pr, Nd, *etc*. Among them, cerium exists in several organisms instead of calcium to accumulate in the bones in very little amounts. Also, human blood, bones, and tissue contain 0.001 ppm, 3 ppm and 0.3 ppm of cerium, respectively. Cerium's biological role has not yet been known, but it is estimated that cerium salts can stimulate metabolism, and be toxic in excessive quantities (11). On the other hand, vanadium is a transition metal in the second period that is found in high concentrations in the earth's crust, fossil fuels, soils, and oceans. Vanadium plays an active role in biological systems due to the diversity of oxidation states changing from 1+ to 5+ (12). The rare earth orthovanadates ($REVO_4$), containing both a rare earth metal and vanadium, have been intensively studied to investigate their biological, physical and chemical properties since their crystal structures were determined (13, 14). The desired cerium- and vanadium-containing compound can be obtained considering this unique structure. Rao and Palanna synthesized cerium orthovanadate for the first time via conventional solid-state ceramic method, in 1995 (15), and investigated electrochemical properties of the material after four years (16). Our research group synthesized cerium vanadate by innovative microwave method using cerium sulfate and vanadium(V) oxide (17), and applied this compound and derivatives against xanthine oxidase as inhibitor (18). Since the 2000s, doping processes of cerium orthovanadate with rare earths, heavy metal, alkaline and alkaline earth metals have been studied (19-29).

In this work, we have investigated a previously unreported microwave-assisted synthesis route for doping cerium vanadate with alkaline earth elements. The host material cerium vanadate has been purely obtained in a short time (10 min) by using microwave irradiation as previously described (15). The commonly presence in nature alkaline earth elements in doping process are chosen to reduce the possible toxic effects of cerium. Taguchi method and ANOVA have been applied to identify the significance of selected parameters related to doping process of cerium vanadate with Be, Mg, Ca, Sr, and Ba ions. The conformation of formation of the doped cerium vanadate derivatives have been controlled via calculation of unit cell volume by Rietveld Refinement analysis using X-ray diffraction data (XRD).

MATERIALS AND METHODS

Mathematical approach of Taguchi

Taguchi approach utilizes orthogonal arrays from design of experiments theory to study a large number of parameters with a small number of experiments. A significant advantage of the Taguchi method is that it performs an experiment with a decreased number of tests, protection the fastness in the analysis (30). The number of experiment can be reduced by using orthogonal arrays. An example typical orthogonal array is shown in Table 1 describing all combination of parameters. That is, nine experiments are to be carried out to study four variables at three levels. Thus, this design reduces 81 configurations to 9 experimental evaluations. Table 2 displays doping process variables and chosen levels for each experiment. Two independent variables at five levels each were selected because of increasing diversity and not applied before: doping element type (Be, Mg, Ca, Sr, and Ba) and doping percentage (2%, 4%, 6%, 8%, and 10%). The following parameters were maintained constant in all tests during experimentation: Temperature of synthesis (800 °C), time of synthesis (2 hours), host material ($CeVO_4$), and starting material types as oxides (BeO, MgO, CaO, SrO, and BaO). Table 3 shows Taguchi orthogonal array for doping parameters of cerium vanadate to decrease number of experiment.

Table 1: Orthogonal array suggested by Taguchi method.

	Variables			
Sample	**A**	**B**	**C**	**D**
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 2: Doping process variables with definite levels.

Processing variables	Level 1	Level 2	Level 3	Level 4	Level 5
Variable 1: Doping element	Be	Mg	Ca	Sr	Ba
Variable 2: Doping percentage (% w)	2	4	6	8	10

Table 3: Taguchi orthogonal array for doped cerium vanadate.

	Variables	
Sample	**Doping percentage**	**Doping element type**
Be1	2	Be
Be2	4	Be
Be3	6	Be
Be4	8	Be
Be5	10	Be
Mg1	2	Mg
Mg2	4	Mg
Mg3	6	Mg
Mg4	8	Mg
Mg5	10	Mg
Ca1	2	Ca
Ca2	4	Ca
Ca3	6	Ca
Ca4	8	Ca
Ca5	10	Ca
Sr1	2	Sr
Sr2	4	Sr
Sr3	6	Sr
Sr4	8	Sr
Sr5	10	Sr
Ba1	2	Ba
Ba2	4	Ba
Ba3	6	Ba
Ba4	8	Ba
Ba5	10	Ba

Optimal working conditions which determined at the end of the experiment must be given very close performance at different conditions and times. The optimization criteria used to realize this can be summarized that variability around performance value must be under control at minimum level. The signal to noise ratio (S/N) is a performance criterion according to Taguchi and classified in three subsections: *lower is better, higher is better or nominal is better*. In this optimization study, the aim is obtaining minimum expansion means the lowest unit cell volume after doping process, the statistical evaluation is chosen as *'lower is better'*. The S/N ratios for the 'lower is better' option was described by the following equation (31):

$$SN_S = -10 * \log\left(\frac{1}{n}.\sum_{t=1}^{n} Y_t^2\right)$$ (Eq. 1)

where t, n, Y stand for experiment number, trial number and performance criteria, respectively. The quantitative effect and the percent contribution of the above mentioned processing parameters to the unit cell volume of doped cerium vanadate was determined using analysis of variance (ANOVA).

SYNTHESIS AND CHARACTERIZATION

All reagents were supplied as analytically pure by Sigma and Merck companies. Ceric sulfate and sodium orthovanadate were employed for preparation of host material cerium vanadate. The preparation of cerium orthovanadate was carried out by grinding $CeSO_4$ and Na_3VO_4 in a molar ratio 1:1 in an agate mortar followed by microwave treatment in a domestic oven (2.45 GHz, 850 W power) for 10 min as described before (15). Doping elements Be, Mg, Ca, Sr, and Ba as metal oxides were weighted according to selected percentage 2, 4, 6, 8, and 10, and added to host material cerium vanadate. Then, regrounded materials were treated at 800 °C for 2 hours to complete the doping process.

Powder X-ray diffraction (XRD) measurements were carried out by Panalytical X'Pert Pro Diffractometer and Cu K_α radiation (λ=1.54056 Å, 40 mA, 50 kV) with a scan rate of 1 º/min with step size 0.02º. The Rietveld analyses of the samples were done by using the High Score Plus (HS+) Program (License number: 92000029). A Siemens V12 domestic microwave oven was used as the microwave source. Protherm conventional furnace was used to complete the doping process.

RESULTS AND DISCUSSION

Figure 1 displays the XRD pattern of doped materials (a) Be, (b) Mg, (c) Ca, (d) Sr, and (e) Ba in 2%, 4%, 6%, 8%, and 10%. The XRD patterns of all samples are completely matched to basic reflections of undoped cerium vanadate. There is no impurity related to doping elements in the XRD pattern. Pure $CeVO_4$ (Inorganic Crystal Structure Database, ICSD: 98-006-6033) crystallized in tetragonal system with unit cell parameters a=b=7.383 Å. c=6.485 Å and V=353.4889 $Å^3$ with space group I 41/amd. Since the crystal structure of cerium vanadate belongs to a tetragonal system, the lattice parameters *a* and *c* can be calculated using following formula.

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$ (Eq. 2)

The unit cell volumes calculated by XRD pattern by Rietveld refinement method from the 25 combinations of processing variables and S/N ratios are given in Table 4. The volume of unit cell is a very important criterion both as a success of doping process and as an indicator of doping an element without expansion.

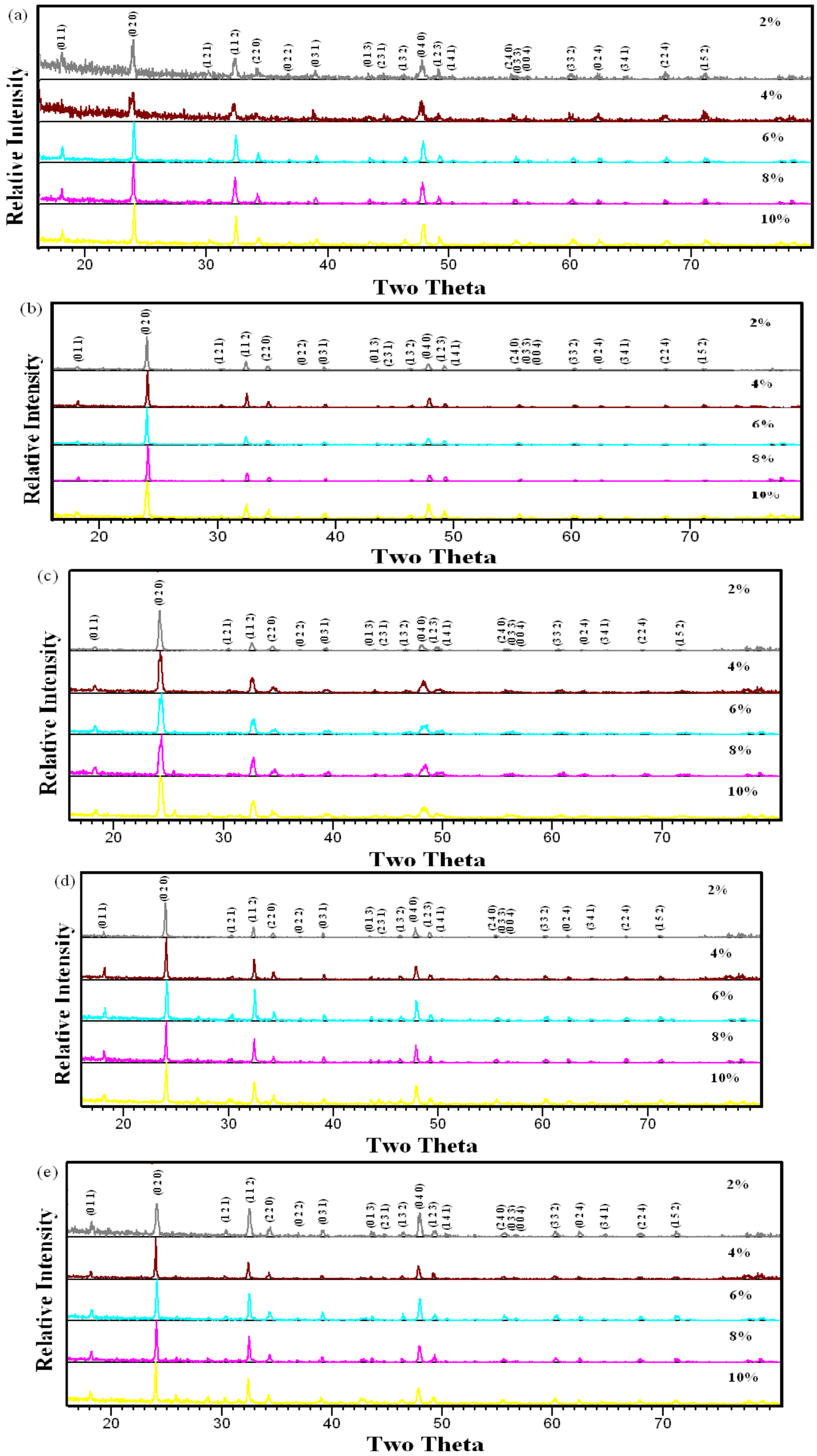

Figure 1: XRD pattern of materials (a) Be, (b) Mg, (c) Ca, (d) Sr, and (e) Ba in 2%, 4%, 6%, 8%, and 10%.

Table 4: Experimental values and corresponding S/N ratios for unit cell volume.

Sample	**Doping parameters**		**Unit cell parameters**		**Unit cell volume**	**S/N ratio**
	Doping percentage (%w)	**Doping element**	**a=b(Å)**	**c(Å)**		
Be1	2	Be	7.4076	6.4816	355.6623	50.019
Be2	4	Be	7.3983	6.4799	354.6722	50.995
Be3	6	Be	7.4011	6.4705	354.4258	50.991
Be4	8	Be	7.3950	6.4912	354.9781	51.002
Be5	10	Be	7.4005	6.4738	354.5586	50.992
Mg1	2	Mg	7.4023	6.4613	354.0491	50.980
Mg2	4	Mg	7.4009	6.4709	354.4412	50.994
Mg3	6	Mg	7.4017	6.4687	354.3916	50.988
Mg4	8	Mg	7.3404	6.5775	354.4148	50.989
Mg5	10	Mg	7.4004	6.4634	353.9782	50.978
Ca1	2	Ca	7.3806	6.4601	351.9055	50.928
Ca2	4	Ca	7.3476	6.4498	348.2096	50.836
Ca3	6	Ca	7.3640	6.4519	349.8856	50.876
Ca4	8	Ca	7.2982	6.4607	344.1227	50.733
Ca5	10	Ca	7.3541	6.4561	349.1675	50.859
Sr1	2	Sr	7.3915	6.4811	354.0902	50.982
Sr2	4	Sr	7.3911	6.4829	354.1505	50.983
Sr3	6	Sr	7.3905	6.4793	353.8976	50.975
Sr4	8	Sr	7.3924	6.4756	353.8807	50.974
Sr5	10	Sr	7.3838	6.4807	353.3362	50.963
Ba1	2	Ba	7.3936	6.4870	354.6207	50.995
Ba2	4	Ba	7.3920	6.4904	354.6488	50.994
Ba3	6	Ba	7.3895	6.4851	354.1236	50.982
Ba4	8	Ba	7.3915	6.4815	354.1138	50.989
Ba5	10	Ba	7.3910	6.4899	354.5272	50.992

Fig. 2 shows the variations in S/N ratio plots of doping process parameters for the unit cell volume. The ANOVA results of unit cell volume are presented in Table 5 which displays doping element type is the most significant parameter on the success of doping process of cerium vanadate with 95 % confidence interval.

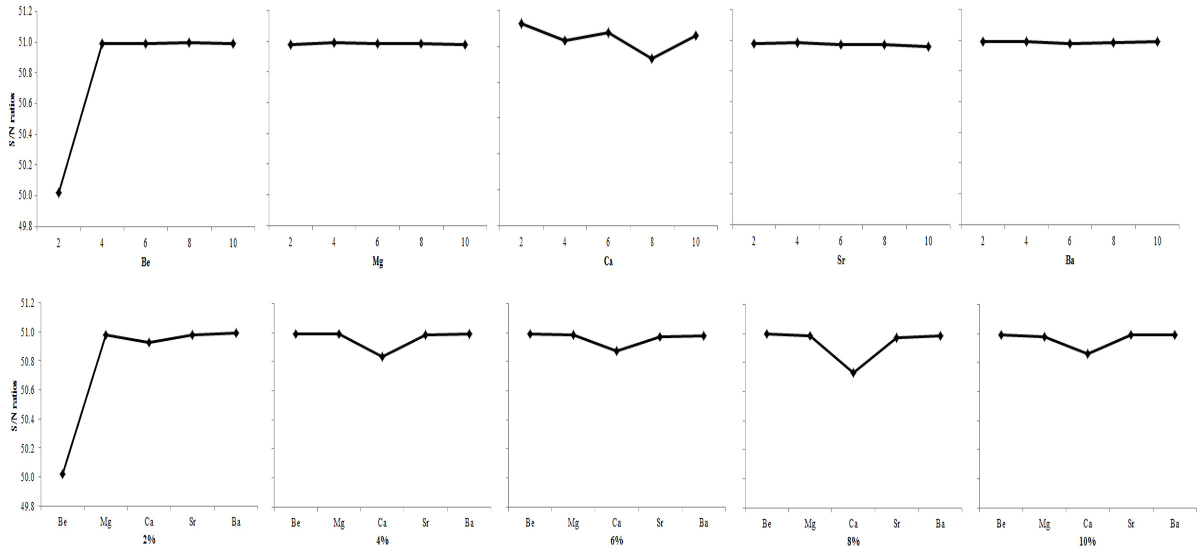

Figure 2: S/N ratios of processing variables for the unit cell volume related to doping percentage and dopant ion type.

Table 5. ANOVA results explaining the significances of doping process parameters on unit cell volume.

Doping process parameters	Degrees of freedom (*f*)	Sum of squares (*S*)	Significance *P* (%)
Doping percentage	5	14.427	5.13
Dopant element type	5	267.072	94.87
Total	8	281.499	100.000

In conclusion, as an optimization technique, Taguchi Method was used to determine the most effective doping process parameters on cerium vanadate doping process with Be, Mg, Ca, Sr and Ba ions. Unit cell parameters and volumes used for comparison were calculated by powder XRD pattern. The type of doping element is the most significant parameter with nearly 95 %. The number of experiments, thereby time and energy consuming were minimized and the significance of the parameters were defined owing to Taguchi method.

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Türkçe Öz ve Anahtar Kelimeler

Be, Mg, Ca, Sr ve Ba İyonları ile Doplanmış Seryum Vanadatın Doplama Süreci Parametrelerinin Optimizasyonu

Gülşah Çelik Gül

Öz: Bu çalışmada, Taguchi yöntemi uygulanarak seryum vanadatın Be, Mg, Ca, Sr ve Ba iyonları ile doplama sürecinin en uygun parametreleri bulunmuştur. Doplama iyonunun yüzdesi ve türü, deneylerin sayısını azaltmak için ortogonal dizi şeklinde uygulanmış optimizasyon sürecinde paramatreler olarak kullanılmıştır. Rietveld Düzeltme analizi X-ışını saçılma verilerinden (XRD) hesaplanan birim hücre hacmi, doplanmış seryum vanadatların oluşumunu doğrulamak için kullanılmıştır. Parametrelerin etkinliğini belirlemek için ANOVA yöntemi uygulanmıştır.

Anahtar kelimeler: Seryum vanadat; metal doplama; X-ışını saçılması; Rietveld düzeltme yöntemi; Taguchi optimizasyon yöntemi.

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