Improvement in Mechanoluminescence intensity of $Ca_2Al_2SiO_7$: Ce by statistical approach

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Abstract--**The mechanoluminescence phenomena of the $Ca_2Al_2SiO_7$: Ce prepared under designed experiment conditions were investigated by fractional factorial design and ANOVA. The mechanoluminescence behavior is shown strongly influenced by the amount of Ca^{2+} and Si^{4+} cations in the crystal. Optimal composition of the oxide compounds was obtained and the mechanoluminescence intensity was fitted with a first order linear model. Intense blue light, which was clearly visible to the naked eye, was emitted when the sample of the $Ca_2Al_2SiO_7$:Ce was pressed.**

Index term --**Mechanoluminescence, Fractional Factorial Design, ANOVA**

I. INTRODUCTION

Mechanoluminescence refers to the light emission from a material induced by stress that caused deformation or fracture of solids. This phenomenon has been known to exist in silica and quartz, sugar, rocks, alkali halide, II-VI compounds and polymer crystals [1]. However, the mechano-luminescence intensities of these existing materials are not strong enough for practical usage.

Recently it was found that rare-earth-doped oxides emit comparatively intensive visible light when stress is applied to these oxides, such as $BaAl_2Si_2O_8$: Ce, $Sr_3Al_2O_6$: Eu, and $SrAl_2O_4$:Eu, etc. In this study, the author explored $Ca_2Al_2SiO_7$: Ce and optimized the mechanoluminescence intensity using Factorial Design and Analysis of Variance (ANOVA) methods. The effects of eight control factors were investigated and compared to determine which factors are significant to affect the mechanoluminescence intensity.

II. BACKGROUND

Mechanoluminescence (ML) materials could be used as stress indicators. The goal of the development of mechanoluminescence materials is to achieve either a luminous paint or film coating that can be applied on the surface of objects under stress, so that the distribution of stress can be visualized.

Even though there have been some efforts to observe stress distribution using the bending or contraction of monotonously shaped mechano-luminescence samples (bar or sphere), it is difficult to see the actual shape of stress distribution in the centered region because of abundant light emission on the contact area with the loading device. In addition, no such effort has ever been made for the conventional samples widely used for mechanical tests such as tensile specimens, compact tension (CT) specimens, etc [1].

Mechanoluminescence is associated with a trap-involved process, in which electrons (or holes) dwell in the trap for some time and then recombine with the luminescence center either by traveling in the conduction band (or valence band) or by electron (or holes) tunneling. As for mechano-luminescence materials, in particular, the recombination process is facilitated by the assistance of dislocation in the crystal [2]. The light emission model has been suggested. Eu^{2+} ions were found to emit a bright green light under 365 nm excitation, while Ce^{2+} has a blue color.

III. EXPERIMENTAL PROCEDURES

Oxides powders were mixed and sintered at various temperatures in different atmospheres. Test samples were made by molding a consistent amount of prepared powders (1.0 g) with 3.5g epoxy resin in a Φ25mm×15mm die. Then the mechano-luminescence intensity was measured with a photomultiplier tube. The test data were in the unit of cps (count per second).

Eight experimental parameters were selected and set at different level as shown in Table 1. Factor

A (atmosphere) was set at two levels (Level0 and Level1) and the rest seven factors were at three levels. They were labeled as Level0, Level1 and Level2. As it is seen from the design of this experiment, $2^1 3^7 = 4374$ trials are required to complete the whole experiment, which is unfeasible in practice. Orthogonal main effect design is appropriate because the size of the design is limited and there are mixed levels [3]. Thus, an L_{18} ($2^1 \cdot 3^7$) orthogonal array design was utilized to reduce the trial number down to eighteen. In this design, the eight main effects are orthogonal, which means that the estimate of one main effect is independent of the other main effects. The data were then analyzed by ANOVA method.

Table 1. Experimental factors and their levels

Factors		Levels		
A	Atmosphere	Ar	Ar+H_2(5%)	-
B	Temperature(°C)	1200	1300	1400
C	Sintering time (h)	1	3	5
D	CeO_2 (mol)	0.00001	0.00005	0.00010
E	Al_2O_3 (mol)	0.009	0.010	0.011
F	SiO_2 (mol)	0.009	0.010	0.011
G	$CaCO_3$ (mol)	0.018	0.020	0.022
H	H_3BO_3 (mol)	0.001	0.002	0.003

In this parameter design methodology, each row of the orthogonal array represents a run, which is a specific set of factor levels to be tested. This L_{18} orthogonal array accommodates one factor at two levels and seven factors at three levels in total eighteen runs, and the underline distribution of each response is assumed to be normal distribution with same variance, which complies with the requirements for ANOVA. However, the complexity of this design, particularly when three level factors are used, will lead to partial confounding of two-factor interactions with main effects. Usually the comfouding pattern is so complicated that even two-factor interactions are not considered, and higher level interactions are assumed negligible. If any two-factor interactions are large, this may end in an incorrect analysis of the experiment [4].

Taguchi argued that it is not necessary to consider two-factor interactions explicitly [5]. It is possible to eliminate these interactions either by correctly specifying the response and design factors or by using a sliding setting approach to choose factor levels. In practice, unless we obtain high level of process knowledge, these two approaches are usually difficult to implement. Therefore, the lack of provision for thoroughly dealing with potential interactions between the experimental factors is a major weakness of this approach.

IV. DATA ANALYSIS AND DISCUSSION

The mechanoluminescence intensities were tested after the L_{18} design of experiment was accepted and the data are shown in Table 2. The intensity varied in a range from 44 cps to 13324 cps, which indicated that the combination of these eight factors largely impacts the mechano-luminescence intensity of this material.

Table 2. L_{18} orthogonal array design and test result

#	A	B	C	D	E	F	G	H	Cps
1	0	0	0	0	0	0	0	0	44
2	0	0	1	1	1	1	1	1	179
3	0	0	2	2	2	2	2	2	1403
4	0	1	0	0	1	1	2	2	273
5	0	1	1	1	2	2	0	0	8379
6	0	1	2	2	0	0	1	1	293
7	0	2	0	1	0	2	1	2	2257
8	0	2	1	2	1	0	2	0	154
9	0	2	2	0	2	1	0	1	7343
10	1	0	0	2	2	1	1	0	198
11	1	0	1	0	0	2	2	1	123
12	1	0	2	1	1	0	0	2	4224
13	1	1	0	1	2	0	2	1	270
14	1	1	1	2	0	1	0	2	7782
15	1	1	2	0	1	2	1	0	1740
16	1	2	0	2	1	2	0	1	13324
17	1	2	1	0	2	0	1	2	792
18	1	2	2	1	0	1	2	0	288

These data were then subjected to ANOVA (in Matlab) to estimate the significance of each factor, as shown in Table 3. And the mean square values were then compared with the residual/error term. According to the F distribution, we can thus obtain the possibility of rejecting a hypothesis that each factor is statistically significant.

Table 3. ANOVA table of ML intensity

Source	S. S. (10^4)	d.f.	M. S. (10^4)	F	P(F)
A. Atmosphere	39.35	1	39.4	6.5	0.13
B. Temperature	283.8	2	141.9	23.5	0.04
C. Sintering time	3.74	2	1.87	0.3	0.76
D. CeO_2	138.8	2	69.40	11.5	0.08
E. Al_2O_3	79.41	2	39.71	6.6	0.13
F. SiO_2	383.6	2	191.8	31.7	0.03
G. $CaCO_3$	1538	2	768.8	127	0.007
H. H_3BO_3	96.28	2	48.14	7.9	0.11
Error	12.08	2	6.04		
Total	2575	17			
R^2	99.5%				
R^2_{adj}	96.0%				

The degree of freedom of the two-level factor is one, while that of the three-level factor is two. The total eight factors would need fifteen degrees of freedom, and left two degrees of freedom for the error term, which is probably unsatisfying for significance estimation. It is observed from table 3 that factor A and factor C have less influence on the intensity of this material. So we pooled these two items into the error term and reran the ANOVA for better estimation of the error term. The new results are shown in Table 4.

Table 4. Adjusted ANOVA table of mechanoluminescence intensity

Source	S. S.	d.f.	M.S.	F	P(F)
B. temp	283.8	2	141.90	12.9	0.01
D. CeO_2	138.8	2	69.40	6.3	0.04
E. Al_2O_3	79.4	2	39.71	3.6	0.10
F. SiO_2	383.6	2	191.80	17.4	0.006
G. $CaCO_3$	1537	2	768.75	69.7	0.000
H. H_3BO_3	96.28	2	48.14	4.4	0.08
Error	55.17	5	11.03		
Total	2576	17			
R^2	98%				
R^2_{adj}	92.7%				

The *F* value of the analysis indicates that the $CaCO_3$ amount is the most important control factor in the examined experimental range. The amount of SiO_2 and sintering temperature are also statistically significant. On the other hand, the *F* statistics of the Al_2O_3 concentrations is 3.6, which is smaller than *F* (2,8:5%) of 4.46, thus the effect of Factor E (Al_2O_3) is not statistically significant in this study. Accordingly, the same conclusion also applied to Factor H (H_3BO_3) and the content of H_3BO_3 is not statistically significant.

Fig. 1. Crystal structure of $Ca_2Al_2SiO_7$

To explain the effects of those significant factors, it is necessary to directly relate these factors to the structure of the material. The structure of $Ca_2Al_2SiO_7$ [6] is shown in Fig. 1. The structure is comprised of layers and spacing between layers. Within each layer structure, the tetrahedral unit is connected via $Al^{3+}$and Si^{4+}. These layers are linked together by the large cation Ca^{2+}, which is surrounded with five tetrahedral and located in irregular octahedrons. It was suggested that the Ca^{2+} and Si^{4+} ions of $Ca_2Al_2SiO_7$ strongly influence the mechanical properties, because the Ca^{2+} ions link the layers and the Si^{4+} ions connect the tetrahedra in the crystal structure, which can explain why the $CaCO_3$ and SiO_2 are significant control factors for the mechanoluminescence intensity. When the sintering temperature is high, the crystal quality is improved.

The individual effect of factors was summarized in table 5 according to the following equations:

$$\Delta y_{ij} = \frac{1}{n}\sum_k y_{ijk} - \bar{y}$$

n -- the run number of each effect at the same level;

$\sum_k y_{ijk}$ -- the sum intensity of factor *i* at level *j*;

$\bar{y}$ -- the average intensity of the 18 runs;

Table 5. Effect of individual factor

Effect	Level 0	Level 1	Level 2	Difference
A	-467.6	467.4	--	935.00
B	-1696.8	396.8	1300	2996.8
C	1.66	175.5	-177.5	353.00
D	-1006.8	-126.5	1133	2139.8
E	-928.2	589.7	338.2	1517.9
F	-1763.2	-48.8	1811.7	3574.9
G	4123.3	-1816.2	-2307.5	6430.8
H	-925.5	862.7	62.5	1788.2

The effect is defined as the difference between the mean value of intensities of same factor at the same level and the grant average, which is about 2726 cps in the measurements. It is shown that effect A and effect C are less significant than the rest other effects. The intensity difference of effect C is only 353, and effect A 's intensity difference is only 935. These observations agree with the ANOVA results.

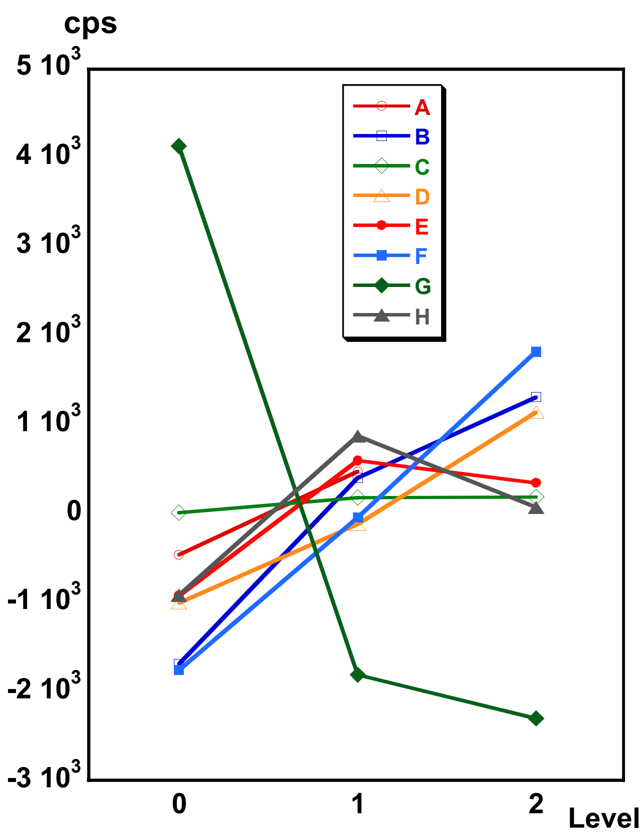


Fig. 2. Individual effect of factors at each level

The mechanoluminescence intensity as a function of individual effect of each factor at different levels is illustrated in Fig. 2. It is easy to see that although most of the effect will lead to a higher mechanoluminescence intensity from Level0 to Level2, factor G actually achieved the highest intensity at Level0 and the lowest at Level2.

The overall optimal intensity of this material could be extrapolated from this plot if we assume that it equals to a first-order linear combination of the effect of all main factors at their maximum values. This is a strong assumption because no interaction terms between the main effects are included in this combination and they are simply neglected. Thus, optimal intensity can be achieved in the following conditions, as shown in table 6. The maximum predicted by this assumption is:

$$cps\_\max = \sum_{i=1}^{8} \max(effect_i)$$

$$= 467 + 1300 + 176 + 1133 + 590 + 1812$$

$$+ 4123 + 863 + 2726$$

$$\approx 13200$$

Table 6. Optimal experimental conditions by first-order approximation

Factor	Level	Real Value
A	1	Sintering atmosphere=Ar+5%H_2
B	2	Sintering temperature=1400ºC
C	1	Sintering time=3 hours
D	2	CeO_2=0.0001mol
E	1	Al_2O_3=0.01mol
F	2	SiO_2 = 0.011mol
G	0	$CaCO_3$ = 0.018mol
H	1	H_2BO_3 =0.002mol

A first-order response surface model is created to test the validity of first-order approximation assumption and to fit these effects by the least squares estimation of parameters. Note that since this is only a first order approximation, higher order of main effects and their interactions were neglected in this model.

In this response surface model, the relationship between the true mean response and eight main factors is established [7]:

$$Y = \beta_0 + \sum_{i=1}^{8} \beta_i X_i + \varepsilon$$

Y is the measured intensity value in each trial with different combination of main factors. β_i is the unknown fitting parameters, and ε is a random error number. If ε has a zero mean, the systematic portion of the model represents the true mean intensity cps, that is,

$$cps = \beta_0 + \sum_{i=1}^{8} \beta_i X_i$$

X_i is coded as the level of factor *i*. Note that factor D (the amount of CeO_2) is not evenly designed.

The coded variables and the measured intensity values are given in table 2. The fitted first-order model for the mechanoluminescence intensity is generated in Matlab:

$$cps = 1000 \times (0.0799 + A \times 0.9351 + B \times 1.4989 - C \times 0.0896 + D \times 1.0699 + E \times 0.6332 + F \times 1.7874 - G \times 3.2154 + H \times 0.4940)$$

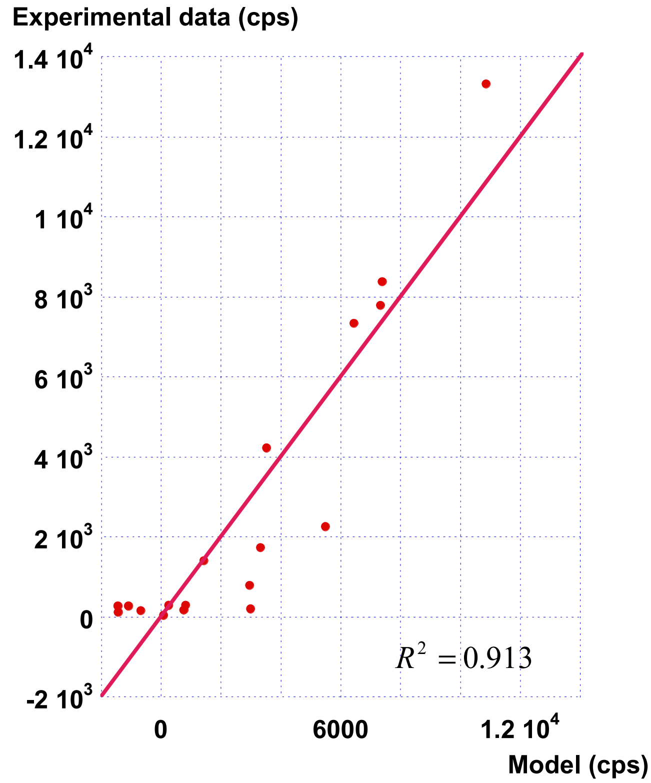
If Factor A and Factor C are excluded from the regression, the linear model becomes:

$$\mathrm{cps} = 1000 \times (0.4579 + \mathrm{B} * 1.4989 + \mathrm{D} * 1.0699 + \mathrm{E} * 0.6332 + \mathrm{F} * 1.7874 - \mathrm{G} * 3.2154 + \mathrm{H} * 0.4940)$$

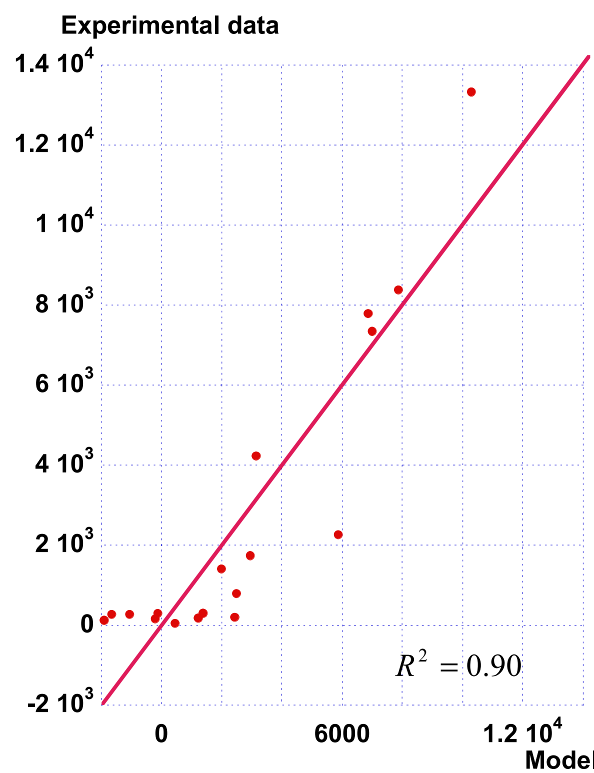
The R^2 values in these two regressions exceed 0.9, which could indicate a good fit in both cases, and the validity of first-order approximation is confident. Although Factor A and C are excluded from the model, the R^2 values only change about 1% which means Factor A and C are not important in the fitting model.

It is also found in this model that the optimal experimental condition is [1 2 0 2 2 2 0 2], and the maximum value of the mechanoluminescence intensity is 12917 cps, which are very close to the experimental result in the $2^1 3^7$ test (run number 16) or result in the linear combination approximation.

The regression model is shown in Fig. 2.



(a). Regression model with all factors



(b). Regression model without Factor A and C

Fig. 2. Comparison of model

After the significances of Factor G, F and B are confirmed, the author tended to fine-tune these three parameters in the vicinity of the "predicted maximum intensity" point. The center point is defined as the composition of $Ca_2Al_2SiO_7$ at the highest mechanoluminescence intensity. Then the contents of $CaCO_3$, SiO_2 and the sintering temperature were changed, and the samples were taken mechanoluminescence measurement as shown in Fig. 3. The starting composition is SiO_2 =0.011mol. When the intensity achieved the highest value, the amount of $CaCO_3$ should be 0.018(1-5%)mol because the ideal $CaCO_3$ shifted 5mol% from the optimal composition of $Ca_2Al_2SiO_7$, which was found in the first-order model. Then the SiO_2 also varied and the highest intensity was gained when SiO_2 is 0.011(1-5%)mol. It is seen that if the sintering temperature rises to 1450ºC, the intensity is the highest.

Fig. 3. Fine-tune the effect of main factors

This above process is essential to compensate the loss of consideration of two-factor interaction during the first-order approximation. For example, both the amount of $CaCO_3$ and SiO_2 should reduce about 5% from the predicted ideal composition, when their effects have to be considered at the same time. Thus the potential weakness of this statistical approach, mixed level experiment design by L_{18} orthogonal array, is inhibited.

Fig. 4. Comparison of mechanoluminescence intensities before and after optimization

As a result, the optimal condition to achieve the maximum mechanoluminescence intensity is listed in table 7. Fig. 4 shows how the intensity changes before and after the optimization process.

Table 7. Optimal experimental conditions

Factor		Real Value
A	Sintering atmosphere	Ar+5%H_2
B*	Sintering temperature	1450ºC
C	Sintering time	3 hours
D	CeO_2 (mol)	0.0001
E	Al_2O_3 (mol	0.01
F*	SiO_2 (mol)	0.01045
G*	$CaCO_3$ (mol)	0.0171
H	H_2BO_3 (mol)	0.002

* important experiment condition.

V. CONCLUSIONS

The mechanoluminescence intensity of $Ca_2Al_2SiO_7$: Ce was improved by statistical approaches. Eight experimental control factors were investigated on their effects on the mechano-luminescence intensity of this oxide material by factorial design and ANOVA. L_{18} orthogonal array was adopted in the design of experiment and the test results show that three main factors, the amount of $CaCO_3$, the amount of SiO_2, and the sintering temperature are statistically important control factors on the mechanoluminescence intensity. Under the first-order approximation assumption, the optimal experimental conditions were explored and the maximum intensity was predicted. Then the interaction effects, particularly between the three significant control factors, were included into the consideration and the final experimental parameters were determined. It is clearly seen that the mechanoluminescence intensity was improved orders of magnitude. The application of statistical approach is successful in the experimental procedure.

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