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Development of Piezoelectric Ceramic Composites

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ABSTRACT

For the past few years, the Materials Technology Laboratory, NRCan, Ottawa and Sensor Technology Ltd., Collingwood, Ontario have been involved in the development of new/improved piezoelectric and electrostrictive sensor and actuator materials and processes for application in a variety of devices. This paper describes the influence of various processing parameters on the sintering, microstructure as well as the dielectric and electromechanical characteristics of lead magnesium niobate – lead zirconate titanate (PMN-PZT) ceramic composite materials. The Taguchi Statistical Design of Experiments methodology has been used to plan, conduct and analyze experimental data. The data indicates that the dielectric and electromechanical properties of these materials are significantly influenced by the material composition and the processing conditions used for the sintering of the composite ceramics.

Keywords: Piezoelectric, Materials, Processing, Properties, Taguchi Statistical Design for Experiments

INTRODUCTION

There has been a growing interest in recent years in lead-based perovskite ferroelectric and relaxor ferroelectric solid solutions because of their excellent dielectric, piezoelectric and electrostrictive properties that make them very attractive for various sensing, actuating and efficient industrial process control applications (1-4). The complex perovskites, lead magnesium niobate ($Pb (Mg_{1/3}Nb_{2/3})O_3$ or PMN), lead titanate ($PbTiO_3$ or PT) and lead zirconate titanate ($Pb(Zr_{(1-x)} Ti_x)O_3$ or PZT) and their solid solutions are of interest because of their superior dielectric and electromechanical characteristics, particularly near their morphotropic phase boundary (MPB). PMN is a relaxor ferroelectric, characterized by strong frequency dependent dielectric maxima (T_m) around –10°C and a diffuse phase transition, whereas PT and PZT are typical ordered ferroelectrics and exhibit a sharp phase transition peak. PMN has a high dielectric constant and substantial electrostrictive coefficient that make it attractive for capacitor and actuator applications (5-7). PMN is known to easily form solid solutions (8) with PT ($T_m \sim 490$°C). PMN-PT solid solutions with approximately 30-35% PT exhibit a MPB and large piezoelectric properties (4, 9-10) and compositions with PT<0.2 have been studied for electrostrictive applications (2). PZT materials near the tetragonal-rhombohedral MPB display very interesting piezoelectric properties and have been widely used for decades for various sensor and actuator applications. Recently, there have been several reports in the literature (11-15) on the development of PMN-PZT based binary systems with a view to producing composite materials with superior properties for various sensing and actuation applications. This paper provides the preliminary results of our investigations on the influence of materials and processing conditions on the microstructure/phase composition and various dielectric and piezoelectric properties of (PMN-PT)-(PZT) composite ceramics.

This study involves the use of Statistical Design for Experiments (SDE) methodology developed by Genechi Taguchi (16-18) to optimize the process of engineering experimentation. SDE is a powerful statistical technique introduced by Sir Ronald Fisher in England in the 1920's for the agricultural industry to study the effect of multiple factors simultaneously on the quality of crop production. Since that time, much development has taken place in SDE area. In a classical SDE technique, one investigates all possible interactions (full factorial design). This could be very time-consuming and expensive. For example, in order to investigate seven factors at two levels, one must conduct $2^7 = 128$ experiments under a full factorial design. The Taguchi design approach provides an economical alternative by utilizing only a small portion of the full factorial array to study the main factors, noise or un-controllable factors and some of the factor interactions. The Taguchi SDE approach can be used to identify the best/optimum condition for a product or process, estimate the influence of individual factors as well as predict the product performance under optimum processing conditions. Perhaps the Taguchi's most significant contribution to SDE methodology is the development of simple standardized "orthogonal arrays" that can be used for a number of experimental situations. The Materials Technology Laboratory at NRCan has been using SDE methodology for the process/product design for over 15 years. In our experience, SDE is the most systematic way to plan, conduct, analyze and interpret experimental data. For details on Taguchi methodology, please see references (16-18).

MATERIALS AND METHODS

The following are the elemental compositions of the composite powders used in this study:

Powder	Composition
0.8PMNPT-0.2PZT	$0.8[0.675Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.325(PbTiO_3)]–0.2[Pb(Zr_{0.52}Ti_{0.48})O_3]$
0.6PMNPT-0.4PZT	$0.6[0.675Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.325(PbTiO_3)]–0.4[Pb(Zr_{0.52}Ti_{0.48})O_3]$

The above compositions contained 1 mole % of excess PbO, to potentially compensate for PbO loss at high sintering temperatures used in this study. In addition, the mixture contained La_2O_3 dopant (<5 mole%). Addition of La is known to improve the ordering of structure (4). The powders were prepared by conventional mixed oxide method via attrition milling of the reagent grade precursor raw materials using zirconia milling media in water. The processing factors and their levels selected in this study to generate a Taguchi L_8 orthogonal array matrix are shown in Table 1. A full factorial design would require 32 experiments to investigate all of the factor interactions. Eight different experimental/trial conditions were produced (see L_8, design matrix in Table 2) using Taguchi experimental design software obtained from Nutek Inc., USA. The influence of these processing conditions on various physical properties of the materials is shown in Table 3. As shown in Table 1, MgO in excess of stoichiometric composition is used as one of the process variables. Previous work in our labs and elsewhere has shown that excess MgO helps in stabilizing crystal structure (reduces pyrochlore phase formation) and improves dielectric and electromechanical properties of the PMN-based ceramics. The powders were calcined at 850°C for 2 hrs. Sintered discs were made by uniaxial pressing of the calcined powders using a PVA binder. X-ray diffractometry was used to analyze the phase compositions (i.e. pyrochlore, perovskite phases) of the sintered parallel-lapped discs using a Rigaku Miniflex x-ray diffractometer. For dielectric and piezoelectric property measurements, the sintered samples were then parallel-lapped using wet SiC powder (600 grit), cleaned in isopropanol using an ultrasonic bath, dried, electroded (using Dupont #4731 silver ink) and re-fired at 600°C for 15 minutes. The density of the sintered samples was calculated by measuring the mass and the volume of the discs. For piezoelectric measurements, samples were poled at 20 kv/cm in a silicone oil bath at 175°C for 10 minutes. The dielectric constant and dielectric loss data were obtained at room temperature at a frequency of 1 kHz using an HP-4192A low frequency impedance analyzer. The radial mode resonance of the samples was analyzed using the method of Sherrit et al. (19). The materials constants of the thickness mode were determined using the method of Smits (20). The piezoelectric d_{33} coefficient was measured using a d_{33} meter.

Table 1: Process factors and levels used to generate Taguchi design matrix

Process Factors	Level 1	Level 2	Level 3	Level 4
Sintering Temperature	1180°C	1210°C	1240°C	1270°C
Sintering Time	2 hrs	4 hrs		
Moles % PZT	20	40		
Wt% excess MgO	1 wt %	3 wt%		

Table 2: Factors matrix/trial conditions produced using Taguchi design approach

Trial Condition #	Sintering Temperature	Sintering Time	Moles PZT	Wt % excess MgO
1	1180°C	2 hrs	20	1 wt %
2	1180°C	4 hrs	40	3 wt%
3	1210°C	2 hrs	20	3 wt%
4	1210°C	4 hrs	40	1 wt%
5	1240°C	2 hrs	40	1 wt%
6	1240°C	4 hrs	20	3 wt%
7	1270°C	2 hrs	40	3wt%
8	1270°C	4 hrs	20	1 wt%

RESULTS AND DISCUSSION

The response data on samples processed using eight different experimental/trial conditions based on Taguchi design is summarized in Table 3. In general the data indicates that the various performance characteristics (physical properties) are significantly influenced by processing conditions. The measured density of the samples displayed only a slight dependence on the trial conditions. Fig. 1 shows a typical example of an x-ray diffraction (XRD) pattern of the sintered and parallel-lapped discs. The major peak intensities of the perovskite (Pr, 110) and pyrochlore (Py, 222) phases were measured and the percentage of the pyrochlore phase was calculated using the following equation:

$$\%Py = 100x\ I(Py)/\ [I(Py) + I\ (Pr)] \qquad (1)$$

The concentration of the pyrochlore phase varied significantly (from 2.37-5.08) under different processing conditions. Since the pyrochlore phase is known to deteriorate the dielectric properties of the PMN based materials, a small or preferably no pyrochlore phase is desirable. To determine the optimum processing condition for each performance characteristic, the average performance is computed for each process factor and plotted for a visual inspection using the Nutek software. Fig. 2 shows the effect of sintering time, mole% PZT and wt% excess MgO on the concentration of the pyrochlore phase. The graph indicates that to minimize the formation of pyrochlore phase, the sintering time and MgO should be kept at level 2 (4hrs and 3 wt% respectively) and mole % PZT should be kept at level 1 (20 mole %). The data analysis also showed that in order to minimize pyrochlore phase formation, the sintering temperature should be kept at level 2 (1270°C). Statistical calculations based on the Analysis of Variance (ANOVA) methodology were performed on the experimental data using Nutek software to determine the % contribution or influence of each process factor on the pyrochlore phase formation (Fig. 3). It was found that sintering temperature, mole% PZT and excess wt% MgO significantly contributed to lowering of the pyrochlore phase formation (% Pyro), while sintering time displayed relatively smaller influence on % Pyro. The statistical analysis of the data also projected that % pyrochlore phase can be lowered to ~1.6% under optimum processing conditions. Figs. 4-8 provide similar statistical data analysis on the dielectric constant, planar coupling coefficient kp, thickness coupling coefficient kt and charge constant d_{33} of the samples. These results are not discussed here due to the size limitation guideline for the publication, but will be discussed in detail during the presentation. The optimum performance conditions and the projected performance under the optimum conditions for various response characteristics are given in Table 4 below. Confirmatory tests on samples processed under optimum conditions provided d_{33} and K^T values close to that projected by the statistical data analysis.

Table 3: Effect of experimental/trial conditions on physical properties

Trial Condition #	Density g/cc	% Pyro Phase	K^T un-poled	K^T Poled	Loss tan δ un-poled	Loss tan δ Poled	kp	kt	d_{33} x 10^{12} C/N
1	7.88	4.33	3638	4564	0.040	0.030	0.47	0.35	514
2	7.80	3.55	2599	3648	0.037	0.029	0.48	0.34	501
3	7.85	2.69	3858	5220	0.033	0.030	0.55	0.38	653
4	7.83	4.49	3108	3838	0.035	0.025	0.52	0.34	497
5	7.80	5.08	3090	3954	0.035	0.026	0.54	0.45	557
6	7.79	2.42	4099	5952	0.040	0.025	0.62	0.45	772
7	7.78	3.06	3316	4504	0.035	0.023	0.58	0.42	629
8	7.73	2.37	4204	5982	0.040	0.025	0.60	0.52	744

K^T= dielectric constant (poled samples), tan δ = dielectric loss**,** kp = piezoelectric planar coupling coefficient, kt = piezoelectric thickness coupling coefficient, d_{33} = piezoelectric charge/strain constant **,**

Table 4. Optimum processing conditions based on statistical analysis of results/data.

Property	Predicted Optimum Conditions, Level				Projected Performance
	Sint. Temp.	Sint. Time	Mole %PZT	Wt % excess MgO	
Density g/cc	1210°C, L2	2 hrs, L2	20, L1	3, L2	7.87
% Pyro	1270°C, L4	4 hrs, L2	20, L1	3, L2	1.6%
K^T (poled)	1270°C, L4	4 hrs, L2	20, L1	3, L2	6235
Loss tan δ	1270°C, L4	4 hrs, L2	20, L1	3, L2	2.11
kp	1270°C, L4	4 hrs, L2	20, L1	3, L2	0.62
kt	1270°C, L4	4 hrs, L2	20, L1	1, L1	0.50
d_{33} x10^{12} C/N	1270°C, L4	4 hrs, L2	20, L1	3, L2	799

CONCLUSIONS/SUMMARY

The results show that the processing factors and the levels selected for various experimental conditions using Taguchi SDE methodology significantly influence the performance of the PMNPT-PZT composite ceramics. The SDE methodology not only identified which factors and their levels (e.g., high/low) are important in optimizing the physical properties of the composite ceramics, but also provided information on the % contribution of each process factor to the properties of these piezoelectric sensor and actuator materials. The purpose of this preliminary investigation was to determine the influence of various processing factors based on SDE methodology. The preliminary results are very encouraging. The factors (e.g., mole % PZT, Wt% MgO) having a large influence on the performance characteristics need to be investigated in detail using an optimization design strategy based on SDE methodology. The high d_{33} values make these materials useful for high strain actuation in smart systems. Further work is underway to study the influence of temperature and frequency on the dielectric and piezoelectric properties of these materials.

REFERENCES

1. Wadhwan, V.K., Pandit, P., Gupta, S.M., "PMN-PT based relaxor ferroelectrics as very smart materials", Material Science and Engineering B 120 (2005) 199-205.
2. Viehland, D., Li, Jie-Feng, McLaughlin, E., Powers, J., Janus, R., Robinsin, H., "Effect of uniaxial stress on the large-signal electromechanical properties of electrostrictive and piezoelectric lead magnesium niobate lead titanate ceramics", J. Applied Physics 95, 4, (2004) 1969-1972.
3. Babooram, K., Ye, Z.G., "Polyethylene Glycol-Based New Solution Route to Relaxor Ferroelectric 0.65Pb $(Mg_{1/3}Nb_{2/3})O_3$- $0.35PbTiO_3$ ", Chem. Mater. 2004, 16, 5365-5371.
4. Winter, M.R., Pilgrim, S.M., "Study on the Effect of Lanthanum Doping on the Microstructure and Dielectric Properties of 0.9Pb $(Mg_{1/3}Nb_{2/3})O_3$ – $0.1PbTiO_3$", J.Am.Ceram. Soc. 84[2] 314-20, 2001.
5. Srout, R., Halliyal, A., "Preparation of Lead-based Ferroelectric Relaxors for Capacitors", Am. Ceram. Soc. Bull., 66[4] 704-11, 1987.
6. Jang, S.J., Nomura, S., and Cross, L.E., "Electrostrictive Behavior of Lead Magnesium Niobate Based Ceramics", Ferroelectrics, 27, 31-34, 1980.
7. Waechter, D.F., Liufu, D., Camirand,. Blacow, M. R. and S.E. Prasad, "Development of high-strain low-hysteresis actuators using electrostrictive lead magnesium niobate (PMN)", Proc. 3rd CanSmart Workshop on Smart Materials and Structures", Montreal, September 28-29, 2000, pp.31-36.
8. Choi, S.W., Shrout, S.J. Jang, Bhalla, A., " Morphotropic Phase Boundary in Pb $(Mg_{1/3}Nb_{2/3})O_3$ –$PbTiO_3$", Mater. Lett. 8 (1989) 253-255.
9. Schmidt, G., Phase Transitions 20, 127 (1990)
10. Uchino, K., "High electromechanical coupling piezoelectrics: relaxor and normalferroelectric solid solutionsSolid State Ionics 108, 43, 1998.
11. Ouchi, H., "Piezoelectric properties and phase relations of Pb(Mg1/3Nb2/3)O3–$PbTiO_3$–$PbZrO_3$ ceramics with Ba or Sr substitutions", *J. Am. Ceram. Soc.*, 1968, **51**, 169–176.
12. Yimnirun, R., Ananta, S., Meechoowas, E. and Wongsaenmai, S., "Effect of uniaxial stress on dielectric properties of lead magnesium niobate-lead zirconate titanate ceramics". *J. Phys. D: Appl. Phys.*, 2003, **36**, 1615–1619.
13. He, L. X., Gao, M., Li, C. E., Zhu, W. M. and Yan, H. X., "Effects of Cr_2O_3 addition on the piezoelectric properties and microstructure of PbZrx Tiy(Mg1/3 $Nb_{2/3})_{1-x-y}O_3$ ceramics", *J. Eur. Ceram. Soc.*, 2001, **21**, 703–709.
14. Cross, L. E., "Relaxor ferroelectrics", *Ferroelectrics*, 1987, **76**, 241–267.
15. Shaw, J. C., Lin, K. S. and Lin, I. N., "Dielectric behavior at morphotropic phase boundary for PMN–PZT ceramics", *Scripta Mater.*,1993, **29**, 981–986.
16. Taguchi, G., Chowdhury, S., Wu, Y, "Taguchi Quality Engineering Handbook", John Wiley & Sons, Inc, New Jersey, USA (2005)
17. Taguchi, G., "System of Experimental Design: Engineering methods to optimize quality and minimize costs", American Suppliers Institute, 1987.
18. Roy, R., "Design of Experiments Using Taguchi Approach: 16 Steps to Product and Process Improvement", John Wiley & Sons, USA (2001).
19. Sherrit, N. Gauthier, H.D. Wiederick, B.K. Mukherjee, "Accurate Evaluation of the Real and Imaginary Material Constant for Piezoelectric Resonator in Radial Mode"; Ferroelectrics, 119:17-32, 1991.
20. J.G. Smits, "Iterative Method for Accurate Determination of Real and Imaginary Parts of Material Coefficients of Piezoelectric Ceramics"; IEEE Trans. On Sonics and Ultrasonics, SU-23:393-402, 1976.

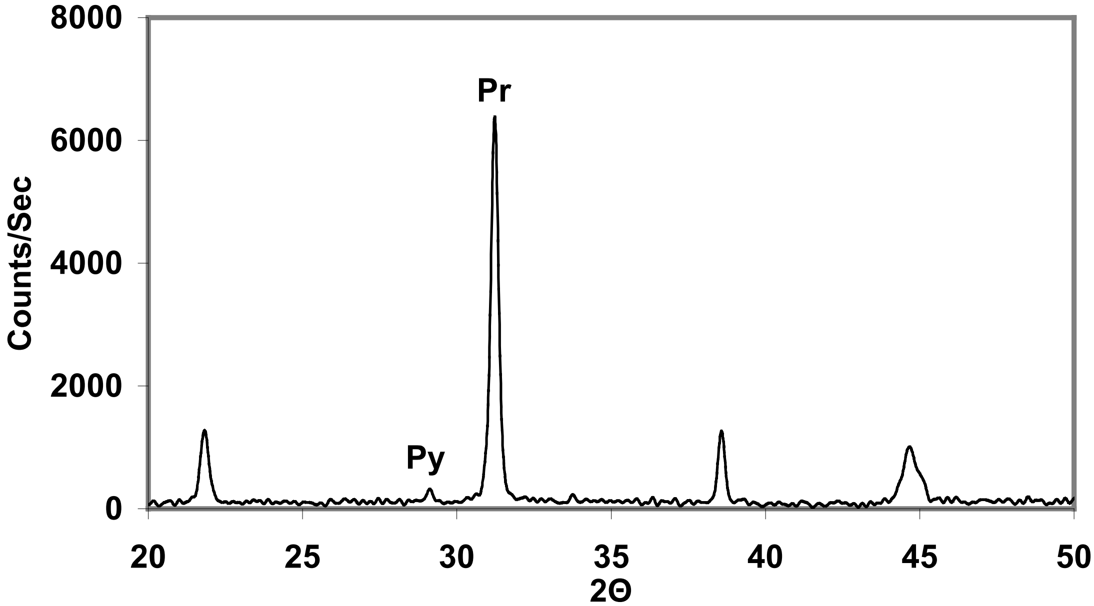

Fig.1. Typical XRD pattern for PMNPT-PZT composite sintered material.

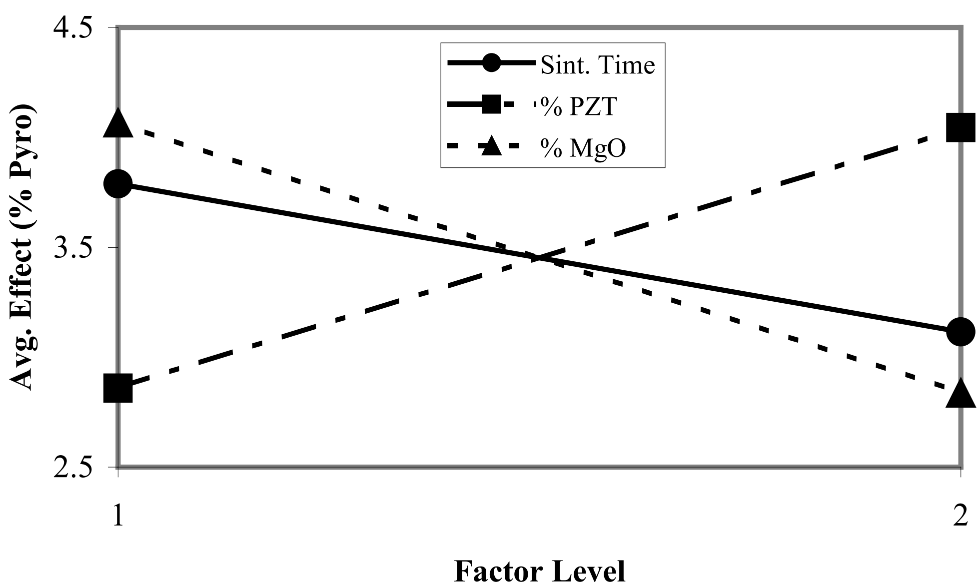

Fig. 2. Effect of process factors on % pyrochlore phase.

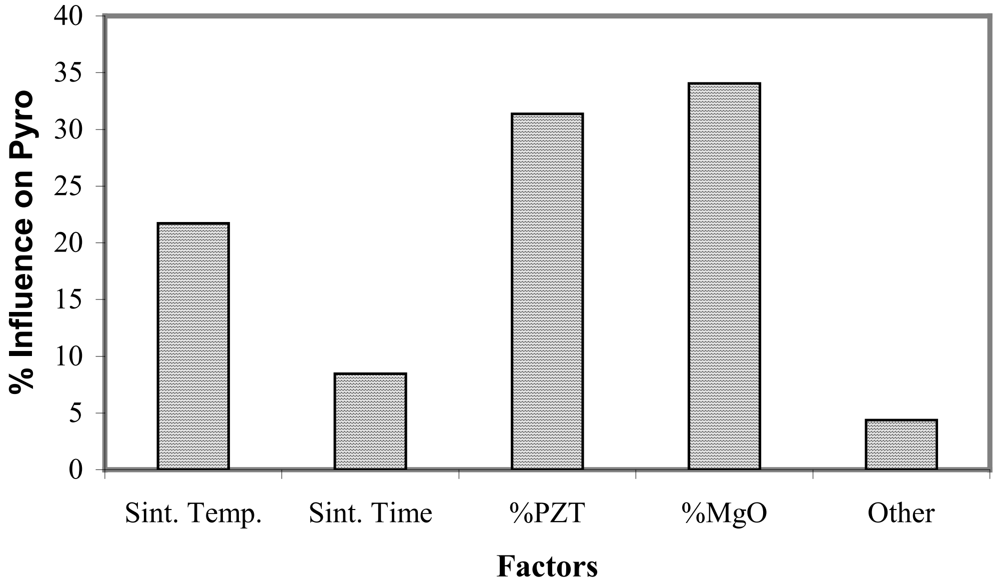

Fig. 3. % Influence of process factors on pyrochlore phase formation

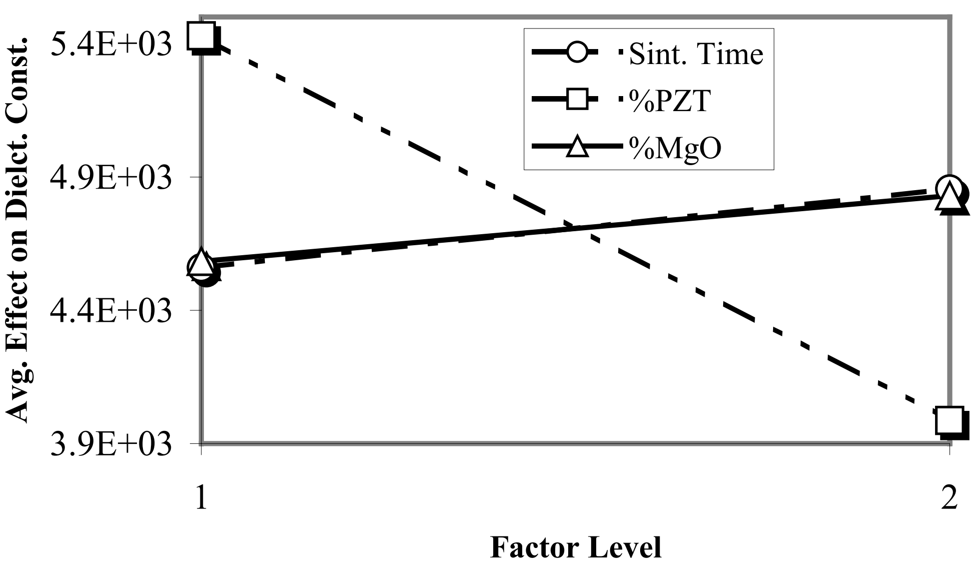

Fig. 4. Effect of process factors on K^T.

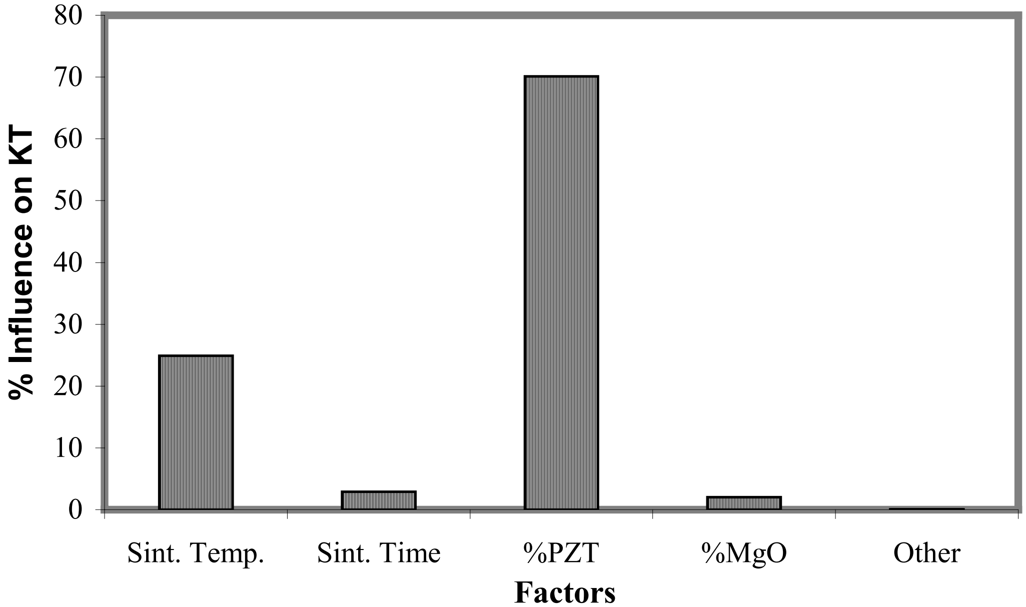

Fig. 5. % Influence of process factors on the dielectric constant (K^T) of poled samples.

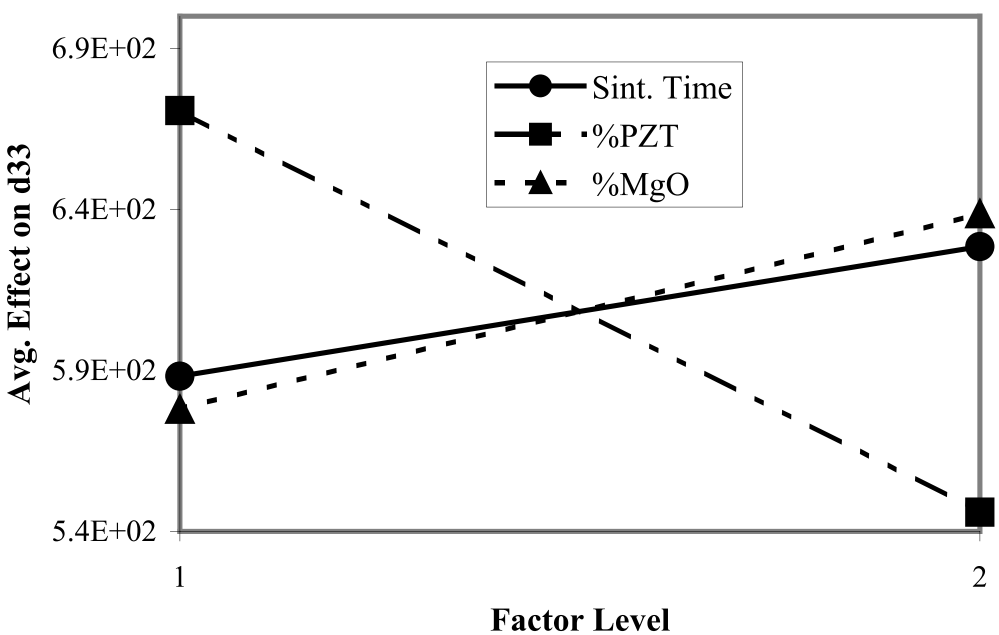

Fig. 6. Effect of process factors on charge constant (d_{33}).

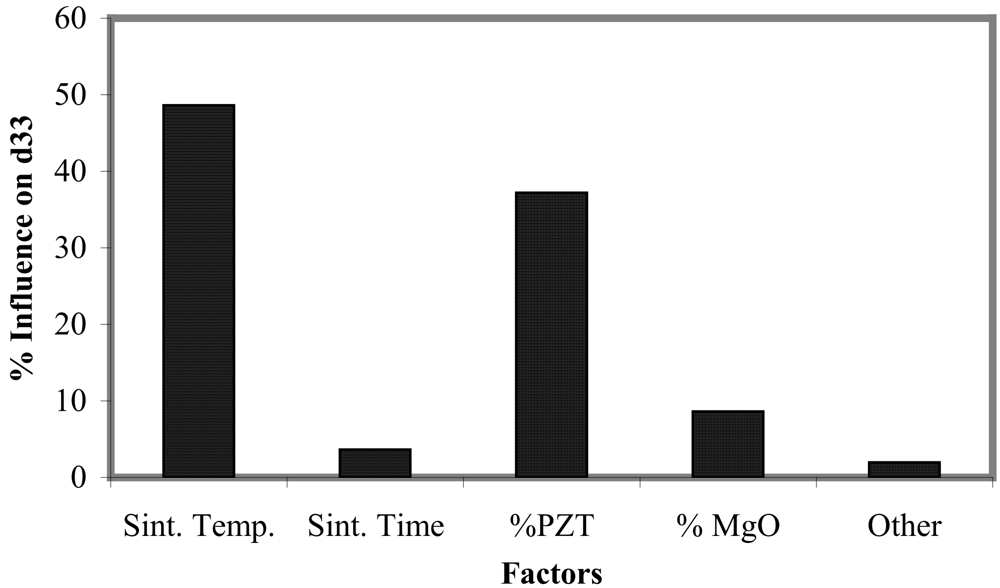

Fig. 7. % Influence of process factors on d_{33}.

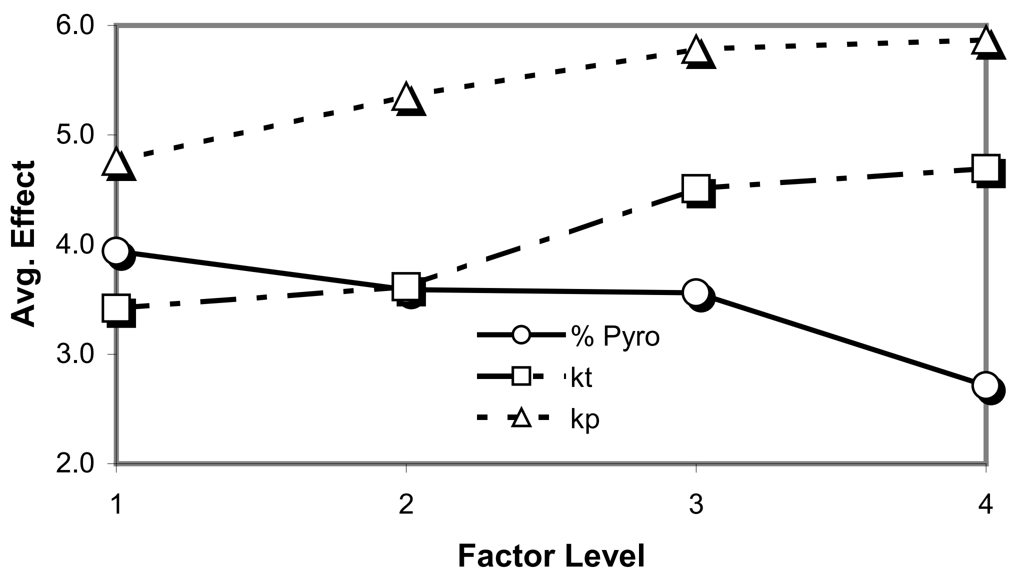

Fig. 8. Effect of sintering temperature on % pyro phase, kt and kp.