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FERROELECTRIC CERAMICS
FOR
DIELECTRIC POWER CONVERSION

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P. C. Held
Research Associate

and

D. A. Payne
Principal Investigator

Department of Ceramic Engineering
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

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Table of Contents

	<u>page</u>
I. Introduction.	1
II. Materials Selected for Development.	3
III. Forming and Processing.	6
IV. Results	9
V. Equipment Considerations.	36
References.	38
Publications.	39

List of Figures

	<u>page</u>
1. Spontaneous Polarization as a Function of Composition in the PZT System.	4
2. Composition Diagram for Materials Prepared in the PSZT System	10
3-8. Curie-Weiss Analysis of Modified PSZT Dielectrics. . . .	13
9-14. Temperature Dependence of Spontaneous Polarization and Coercive Field for Modified PSZT Dielectrics	20
15-18. Temperature Dependence of Electrical Resistivity for Modified PSZT Dielectrics.	27
19. X-ray Diffraction Data for Sputtered PZT Films	34
20. X-ray Diffraction Data for HS-23-55.	35
21. Conductance Loss Loops in HS-23-55	37

List of Tables

1. Curie-Weiss Data for Motorola PSZT 5396B	33
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FERROELECTRIC CERAMICS FOR DIELECTRIC POWER CONVERSION

I. INTRODUCTION

A. Dielectric Power Conversion

1. Concept

Dielectric power conversion is a proposed method of transforming thermal energy into electric power directly, by using a dielectric material as the heat exchange medium. Previous analyses¹⁻⁴ indicated differing theoretical efficiencies for this process, depending upon the nature of the dielectric material, the reversibility of the cycle, and the concept of staging. The highest efficiencies per stage/section were approximately 1 to 2% when optimistic material parameters were used in the calculations.

2. Figure of Merit

A figure of merit, proportional to efficiency, is given by the expression $M = \beta P_s^2 / 4C_p$, where β is the temperature dependence of the reciprocal dielectric susceptibility above the Curie point (and is the same as the first coefficient in the Devonshire polynomial), P_s , the spontaneous polarization, and C_p , the heat capacity at constant polarization. The polarization parameter squared (P_s^2) dominates the figure of merit for most ceramic materials. This charge must be released at several different temperatures so as to successfully operate a multistage converter. Additional material constraints (unrelated to thermodynamic efficiency) are requirements for high resistivity, low coercive fields, fast switching times, chemical stability, good heat transfer characteristics, producibility, and reasonable cost.

Both theoretical and practical requirements have led to a materials development program which is the subject of this report.

B. Materials of Possible Use

1. Early Defined Materials

It was recognized early on in this program that ferroelectric materials with high spontaneous polarizations were good candidate materials for dielectric power conversion. They were previously reported,^{5,6} and included several niobates and tantalates, BaTiO_3 , lead zirconate-titanates (with additives of lanthanum and tin), KDP, NaNO_2 , and lead germanate.

2. Additional Materials

Current and older literature is continually being evaluated for additional materials of possible interest. Chief among these were $\text{Bi}(\text{Na},\text{K})\text{Ti}_2\text{O}_6$ ⁷ and various rare-earth titanate-niobates,⁸ which were reported to have high spontaneous polarizations. Several mixed oxide layer structure⁹ compounds were also evaluated, but the data did not show enough encouragement for continuation of the work.

II. MATERIALS SELECTED FOR DEVELOPMENT

Materials selected in this program were those which could be expected to have useful Curie temperatures (T_c), resistivities (ρ), coercive fields (E_c), and Devonshire coefficients (β).

A. PZT

A great deal of information is available in the literature on the lead-zirconia-titania system (PZT), both across its compositional range and with additives. In the undoped material, three areas of interest exist:

(i) PbTiO_3 , with¹⁰ a P_s as high as 0.81 C/m^2 , but with high E_c and a destructive phase transformation at T_c ,

(ii) Crystalline solutions near the morphotropic boundary, which are reported to maximize polarization at 56 m% PbZrO_3 (Figure 1),¹¹

(iii) Crystalline solutions near the antiferroelectric/ferroelectric boundary (AFE/FE), where field enforced transitions might enhance the operation of the conversion cycle.

In all these cases, additives are required to modify T_c , E_c , ρ , P_s , and β .

B. $\text{Bi}(\text{Na},\text{K})\text{Ti}_2\text{O}_6$

Jaffe et. al.⁷ reported for $\text{Bi}(\text{Na},\text{K})\text{Ti}_2\text{O}_6$ a P_s value of 0.38 C/m^2 , with an E_c of 73 kW/cm and a T_c of 315 to 370°C . Earlier worker¹² reported lower values of T_c , E_c and P_s . This system indicated the possibility of property manipulation, and seemed worthy of investigation.

C. ReTiNbO_6

P_s values on several rare earth titano-niobates, as determined by non-hysteresis measurements, were reported by Russian workers⁸ to be extremely high. Crystallographic structure determinations indicated linked octahedral chains that could displace for high polarizations.¹³⁻¹⁴ Reported resistivities were not high, but could be improved by doping.

FIGURE 1. Spontaneous Polarization as a Function of Composition in the PZT System.¹¹

D. Tantalates and Niobates

With the exception of antiferroelectric NaNbO_3 , most of the tantalates and niobates are strongly ferroelectric (except KTaO_3). Most of these materials have high T_c and E_c (e.g., LiTaO_3). Practical problems occur on sintering, and require hot pressing and stoichiometry control to achieve end point density.

E. Thin Films

Thin films have advantages over bulk ceramics by requiring low coercive voltages, and are of forms which require no further machining.

Thin films were sputtered at Iowa State University, evaluated at the University of Illinois, and supplied to Power Conversion Technology.

III. FORMING AND PROCESSING

Due to the number of materials evaluated in this program, various processing techniques were necessary.

A. Sintering

Sintering is a process of densification for powder compacts (below the melting point) by one or more atomistically based mass transport processes, such as diffusion or vaporization-condensation. The driving force is the reduction of available surface free energy. Considerable variations in densification behavior may be possible and attributable to source materials, stoichiometries, atmospheres, temperatures, particle size and shape, and initial forming conditions.

B. Atmosphere Control

Sintering is complicated if the material being densified tends to vaporize or react selectively with the container. Usually, low melting point constituents like PbO , CdO , Bi_2O_3 , B_2O_3 , V_2O_5 , and alkali oxides tend to have high activities. For example, it is necessary to overcome the vaporization loss of PbO for densifying PZT ceramics. Lead oxide vapor pressures vary by many orders of magnitude over the normal firing range of PZT's, and by nearly two orders of magnitude over the compositional range of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$. This tendency to loose PbO may be prevented, by saturating the vapor with a material having a higher lead oxide vapor pressure than the PZT being sintered.

C. Hot Pressing

Alkali niobates and tantalates are subject to loss of volatile alkalies, which is detrimental to the structural integrity of the material. Hot pressing aids in the densification of the refractory mixed oxides. Hot pressing also aids in the densification of PZT compositions. Simultaneous

application of pressure reduces firing temperature by at least 100°C. The result is a fine grain dense microstructure. While fine grain sizes (e.g., 1 μm) are desirable in most ceramic materials, there is a preponderance of evidence that indicates PZT ceramics have higher polarizations only when they have large grain sizes (e.g., 10 μm). Thus, a two stage firing process was developed, where (i) hot pressing initially eliminated porosity and densified the ceramics, and (ii) a final high temperature heat treatment was used to promote and control grain growth.

D. Liquid Phase Sintering

Sintering in the presence of a liquid phase is used to obtain densification at greatly reduced temperatures. Such techniques are categorized as to whether the liquid is homogeneous or heterogeneous with its host. Heterogeneous liquids react little, if any, and usually require high volume fractions to be effective. The mechanism of densification is rearrangement of particles. Homogeneous, or reactive liquids, can enhance diffusion rates, and achieve densification at low concentrations. This type of liquid may sometimes be removed in sintering by volatilization.

Many practical ceramic processing methods combine one or more of the aforementioned techniques, and this was the case in the present research and development program.

E. Wafering

Large solid sintered samples were sliced into 0.025 cm sections by a diamond saw, and polished by hand on polishing paper. The resulting wafers were uniform in thickness, ± 0.0015 cm.

F. Electroding

Electrodes were applied to thinned ceramic wafers by sputtering, vaporization, firing on fritted silver mixtures, and by application of various

silver loaded glues and epoxies. Each type of electrode application was found to have various advantages and disadvantages. Vaporization provided the least possible contamination, but was slow and required masking. Sputtering was fast and free from contamination. Both of these techniques deposited only a small amount of electrode material on the ceramic, which led to continuity and contact problems. Fired on electrodes were rugged, and sometimes reacted significantly with the ceramic. The firing process could change the stoichiometry of the dielectric material. Silver loaded epoxies and glues were easy to apply and were rugged, but had temperature limitations. They could never be used in a high temperature heat engine.

IV. RESULTS

A. In House Materials

Several classes of materials were fabricated by various sintering techniques, with the greatest emphasis placed on PZT dielectrics.

1. PZT

Figure 2 summarizes most of the compositions and dopants evaluated to date, but does not include high lead titanate compositions which are reported later in this section. The most successful firing results were obtained when 25 to 30 w/% PbO or Pb_3O_4 was added to the material before sintering. Powder pellets were pressed at 100-300 MPa, with water or PVA as a binder. Higher forming pressures did not correlate with final fired density, and introduced cracks. Lower forming pressures were preferred. Pressed pellets were set on coarse zirconia powder in an alumina crucible and surrounded by an expendable mixture of PbZrO_3 and PbO powders, which provided a high PbO activity in the early stages of sintering (when PbO was a liquid). Refractory cement sealed the crucible, which was placed in a furnace and heated at 160°C/hr up to 960°C and held for two hours. After this soaking period, the temperature was raised to $1140\text{--}1150^\circ\text{C}$ and held for an extended time of 20 hours. This high temperature soaking period was to drive off excess lead oxide into the zirconia powder and porous alumina crucible. After furnace cooling, the samples were wafered with a diamond saw, polished, and electrodes applied.

Electrical measurements started with capacitance and dissipation factor as a function of frequency to determine if there were any contact resistance problems. Three major electrical tests were made on most of the materials:

- (i) Capacitance and D.F. were measured as a function of temperature above the Curie point. This data yielded the first

FIGURE 2. Composition Diagram for Materials Prepared in the PSZT System.

Devonshire coefficient (β) from the slope of the inverse dielectric constant versus temperature plot. Representative relationships are illustrated in Figures 3-8.

(ii) Polarization and coercive field measurements were made as a function of temperature in a modified Sawyer-Tower circuit at 60 hertz. Representative results are illustrated in Figures 9-14. Note, the weak field Curie point is lower than the temperature at which the spontaneous polarization goes to zero.

(iii) Resistivity was determined as a function of temperature and voltage. Typical results are illustrated in Figures 15-18. Electrical resistivity is a critical parameter for estimating energy losses in the proposed heat engine, especially at high temperatures. It is also important as an estimator of dielectric reliability for extended periods of time. Samples with fired on electrodes of composition 1, 2, 3, 12, 13, 29, 30, 31, 32, 33, 34, 35, 36, 42, 44, 45, 46, and 48 were supplied to Power Conversion Technology, La Jolla, California.

2. Lead Titanate

Reported values of 0.81 C/m^2 for P_s in single crystal PbTiO_3 have not been substantiated for polycrystalline ceramics. This is probably due to the destructive nature of the phase transformation, and cracking of sintered compacts on cooling through T_c . Another problem is the high coercive field. Our work investigated the possibility of reducing transformation strain effects, reducing coercive field, and increasing electrical resistivity. Additives included $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and PbO as sintering aids and boundary phase materials ($< 10 \text{ w\%}$), as well as La_2O_3 and Nb_2O_5 as substitutional defect compensators ($< 5 \text{ m\%}$). Strong ceramics were obtained, which did not crack on cooling with D.F.'s $< 4\%$. However, the coercive fields were high and the spontaneous polarizations low. The refractory nature of the compensators made

FIGURES 3-8. Curie-Weiss Analysis of Modified PSZT Dielectrics

FIGURE 3.

FIGURE 4.

FIGURE 5.

FIGURE 6.

FIGURE 7.

FIGURE 8.

FIGURES 9-14. Temperature Dependence of Spontaneous Polarization and Coercive Field for Modified PSZT Dielectrics

FIGURE 9.

FIGURE 10.

FIGURE 11.

FIGURE 12.

FIGURE 13.

FIGURE 14.

FIGURES 15-18. Temperature Dependence of Electrical Resistivity for
Modified PSZT Dielectrics

FIGURE 15.

FIGURE 16.

FIGURE 17.

FIGURE 18.

it difficult to obtain theoretical density. Additions of lead germanate consistently showed an optimum firing condition of 1100°C, with overfiring above this point. PbO worked best as a densifying agent at 5 w/%, rather than 10 w/%. Additional tests are planned with B_2O_3 and V_2O_5 as fluxes,¹⁵ and dopants of larger ionic radii for the reduction of coercive field.

3. Rare Earth Titanoniobates

A great deal of interest was generated by a Ukrainian article⁸ on rare earth titanoniobates. These materials were complex chains of titania-niobia octahedra with interleaved rare earth oxide layers. Discharge measurement into an electrometer indicated high "spontaneous polarizations", especially for the ceria, terbia, and lanthanum varieties. We synthesized calcined powders of the three most attractive materials. X-ray diffraction patterns agreed well with accepted ASTM card files ($TbNbTiO_6$ 20-1256, $CdNbTiO_6$ 15-846, and $LaNbTiO_6$ 20-1367). Pressed pellets of the calcined material were fired at various temperatures, up to the point of overfiring when bloated, black samples resulted. The best firing temperatures were 1300, 1333, and 1450°C respectively, for La, Ce, and Tb modifications. The fired structure consisted of equaxed grains up to 20 microns. Electrical measurements indicated no ferroelectric hysteresis loops for any of these materials. The dielectric strengths were high, with $LaTiNbO_6$ holding a field of 60 Kvac/cm for several days without breakdown. Weak field dielectric measurements showed a continuing increase in D.F. with temperature, and Curie points were not identified. The materials do not seem to be ferroelectric in the sense of having a reversible component of polarization, and a dielectric anomaly.

4. Other Tantalates and Niobates

Substituted tantalates and niobates were sintered in air with the aim of reducing the Curie point to levels usable in a heat engine. $KNbO_3$

($T_c \sim 418^\circ\text{C}$) and LiTaO_3 ($T_c \sim 618^\circ\text{C}$) were doped with ions to reduce the Curie point. All the KNbO_3 ceramics crumbled or appeared mottled after firing. LiTaO_3 ceramics appeared to be mechanically sound and dense with 16% linear shrinkage. However, even the densest LiTaO_3 composition had high D.F.'s. Work currently in progress on hot pressing niobates and tantalates indicates improved stability and densification.

B. Out of House Materials

1. Material Uniformity Study

A question of the uniformity of various ceramics was raised during a recent review of the project. To test the uniformity, a series of six slices were taken from two Motorola PSZT ceramic boules, and the weak field Curie point measured precisely for each of the slices. Experimentally, it was found necessary to make the measurements in a temperature stable silicone oil bath. The results are reported in Table 1, and indicate good uniformity throughout the boule. When compared with measurements reported last year from another boule of the same material, these values of weak field Curie point are in good agreement.

2. Thin Film Results

Thin films of PZT sputtered at Ames Laboratory were evaluated. X-ray diffraction analysis indicated little crystallinity within the films. The accepted development of a perovskite structure in sputtered films generally proceeds as an amorphous/pyrochlore/perskovite transformation, with increasing substrate temperature, annealing time, and thickness.¹⁶ Figure 19 summarizes observations from reference 15, while Figure 20 illustrates results obtained for samples obtained from Ames. SEM photomicrographs indicated no grain structure. Polarization-field loops for these films were dominated by conductance loss rather than displacement of polarization charge

Table I

Curie-Weiss Data for Motorola PSZT 5396B
(oil bath, 1KHz)

<u>Sample</u>	<u>β (Mvm/C°K)</u>	<u>Correl Coeff.</u>	<u>θ (°C)</u>	<u>T_C^H (°C)</u>	<u>T_C^C (°C)</u>
1	0.413	0.995	151.0	179.0	177.0
2	0.256	0.996	146.5	178.5	177.0
3	0.356	0.994	152.0	179.4	178.0
4	0.336	0.997	151.0	179.5	177.0
5	0.361	0.996	149.5	176.0	176.0
6	0.313	0.999	153.0	177.0	176.0

NOTE: Only T_C (heating or cooling) not a function of errors in geometry parameters.

FIGURE 19. X-ray Diffraction Data for Sputtered PZT Films.¹⁵

FIGURE 20. X-ray Diffraction Data for HS-23-55.

(Figure 21). No saturable ferroelectric loops were obtained. The films sustained large electrical fields for their thickness.

V. EQUIPMENT CONSIDERATIONS

We have developed hot pressing equipment which should improve our capability for forming PZT ceramics and make it possible to obtain dense stable niobates and tantalates. This equipment uses double walled press dies of alumina in silicon carbide, and is based on techniques developed by Motorola for electrooptical PLZT ceramics. Production of thin layers depends on wafering with diamond saws and polishing. Should large quantities of material be needed for a demonstrable engines of several KW, then considerable improvements must be made in thin layer technology. The method of tape-casting is anticipated.

FIGURE 21. Conductance Loss Loops in HS-23-55.

REFERENCES

1. Fatuzzo, E., Kiess, H., and Nitshe, R., J. Appl. Phys., 37, 510-516, (1966).
2. Van der Ziel, A., J. Apply. Phys., 45, 4128, (1974).
3. Gonzalo, J. A., Ferroelectrics, 11, 423-430, (1976).
4. Drummond, J. E., Proc. 10 Intersociety Energy Conversion Engineering Conference, IEEE, N.Y., p. 569-575, (1975).
5. Payne, D. A., Annual Report, C00-4679-1, (1979).
6. Tuttle, B. A., Payne, D. A., and Mukherjee, J. L., Ferroelectrics, 27, p. 219-222 (1980).
7. Jaffe, B., Cook, W. R., and Jaffe, H., Piezoelectric Ceramics, p. 205, Academic Press, (1971).
8. Sych, A. M., Klenus, V. G., and Nekrasova, I. M., Inorganic Materials, 11, 386-389, (1977).
9. Isupov, V. A., Smirnova, E. P., Isupova, E. N., Zaitseva, N. V., Pikush, L. P., and Smolenski, G. A., Sov. Phys. Sol. State, 18, p. 835-836, (1977).
10. Venevtsev, Yu. N., Zhdanov, G. S., Solov'ev, S. P. and Ivanova, V. V., Kristallografiya, 4, 255-256, (1959).
11. Berlincourt, D., Cmolik, C., and Jaffe, H., Proc. IRE, 48, 220-229, (1960).
12. Smolenski, G. A., Isupov, V. A., Agranovskaya, A. I. and Krainik, N. N., Fiz. Tverd. Tela, 2, 2982-2985 (1960).
13. Aleksandrov, V. B., Kris. Stru. Esh. Doklady Akad. Nauk. SSSR, 142, p. 181-184 (1962).
14. _____, ibid., 132, p. 669-672, (1960).
15. Wittmer, D. E., Ph.D. Thesis, University of Illinois (1979).
16. Nakagawa, T., Yamaguchi, J., Usuki, T., Matsui, Y., Okuyama, M., and Hamakawa, Y., Jap. J. Appl. Phys., 18, p. 897-902 (1979).

FERROELECTRIC MATERIALS FOR DIELECTRIC POWER CONVERSION

by

B. A. TUTTLE, D. A. PAYNE AND J. L. MUKHERJEE
Department of Ceramic Engineering
and
Materials Research Laboratory
University of Illinois at Urbana-Champaign
Urbana, Illinois 61801

ABSTRACT

Ferroelectric materials were evaluated as possible candidates for dielectric power conversion in the proposed Drummond solid state heat engine. Ceramic materials having the highest calculated efficiencies were PbTiO_3 and LiNbO_3 . The best organic materials were KDP and NaNbO_3 . Considerations outside the realm of thermodynamics limit the practical use of many organics and single crystals. The best commercially available materials appeared to be members of the PZST solid solution series, especially those exhibiting field enforceable antiferroelectric-ferroelectric switching over wide temperature differentials. Estimates are given for conversion efficiencies in terms of a figure of merit which was calculated from spontaneous polarization (P_s), inverse Curie constant (β) and heat capacity (C_p) data.

INTRODUCTION

A new type of heat engine was disclosed in 1975 by J. E. Drummond,¹ in which the working substance was not a gas or fluid (as in the conventional type of heat engine), but a ferroelectric dielectric operating around its Curie temperature. It was claimed that high conversion efficiencies could be expected for the proposed solid state heat engine, if Carnot cycles were used in conjunction with multistage converters. This would realize improvements over previously reported attempts^{2,3} to directly convert thermal energy into electric power by ferroelectric heat exchangers. At or about the same time, other investigators were involved with the choice of ferroelectric materials for energy converters⁴ and the concept of extracting heat by multistage elements.⁵ This paper is concerned with an evaluation of possible candidates for dielectric power conversion systems.

The basis for energy conversion is the electrocaloric effect that occurs in all dielectrics that exhibit a temperature dependence of susceptibility. The effect is particularly significant at ferroelectric transitions, especially when the spontaneous polarization is field enforceable. Ferroelectric insulators with high transition temperatures, spontaneous polarizations and electrocaloric coefficients are initial candidates for dielectric power conversion systems. Also, thermal impedance should be low, and materials with low specific heats (c) and density (ρ) are especially required. This paper is concerned with estimates of conversion efficiency (η) based upon a proposed figure of merit (M)^{1,6},

$$M = \frac{\beta P_s^2}{4C_p}$$

MATERIALS

The figure of merit M , which is an approximate solution of conversion efficiency, is dependent on the following material parameters:

(i) It is directly proportional to β , the inverse Curie constant, which is related to lattice softening and is thus relatively constant for materials of the same structure type and elastic properties. β values will not change significantly within a family of materials (e.g., perovskites), even though P_s and T_c may vary considerably.

(ii) The figure of merit M depends directly upon the square of the spontaneous polarization (P_s^2). Carnot efficiency also becomes greatest at high operating temperatures and thus the initial search for candidate materials was concerned with those materials which had high values of P_s and T_c . Unfortunately, there is a lack of information in the literature on values of P_s at T_c . Therefore, we took as a first approximation values of P_s at room temperature. Recognizing the limitation, we summarize in Fig. 1 the relationships existing between P_s at 300°K and T_c , for a large number of materials. The diagram can be separated into regions that correspond to various families of ferroelectric materials. For example, members of the $YMnO_3$ family have high transition temperatures but low spontaneous polarizations ($<0.1 \text{ C/m}^2$); whereas, members of the $LiTaO_3$ - $LiNbO_3$ family have high P_s values ($\sim 0.5 \text{ C/m}^2$) in similar temperature regions. Layered structure compounds (with the possible exceptions of Bi_2WO_6 and $Bi_4Ti_3O_{12}$) have lower spontaneous polarizations. So do $Pb_3(Ge,Si)_3O_{11}$, KNO_3 , $NaNO_2$, KDP, TGS, and other organic sulphates and alums. The most attractive groups of materials based upon P_s and T_c data alone are the perovskites and tungsten bronzes. Examples include the barium strontium niobate series (BSN), and various lead

FERROELECTRIC MATERIALS FOR DIELECTRIC POWER CONVERSION

zirconium titanate (PZT) solid solutions, containing tin (PZST) and lanthanum (PLZT). The arrow on PbTiO_3 is for the uncertainty that exists in the literature for P_s measurements and calculations.

(iii) The remaining parameter in the figure of merit is the inverse dependence on heat capacity at constant polarization (C_p) which can be minimized by considering less dense materials like organic ferroelectrics. However these materials have lower P_s and T_c values than the previously mentioned ceramics. Stability could be an additional problem for organic ferroelectrics, especially with respect to thermal decomposition and dissolution in heat exchange media. These problems aside, we evaluate figures of merit from material considerations.

ESTIMATES OF EFFICIENCY

Estimates of conversion efficiency were calculated from material parameters and are listed in Table 1. The last two columns represent upper ($\eta_{\max}$) and lower ($\eta_{\min}$) bounds, due to the temperature dependence of spontaneous polarization and specific heat. If data at the transition temperature were unavailable, values at the next best temperature were taken. (That is, the temperature given in parentheses.)

Ceramic materials having the highest polarizations and efficiencies were LiTaO_3 , LiNbO_3 , and PbTiO_3 . Their respective efficiencies were 0.7, 3.4, and 6.1% per layer.

TABLE 1. Estimates of conversion efficiency from figure of merit calculations.

Material	T_c (°K)	d (Mg/m ³)	β (MVm/C°K)	$P_s(298^\circ\text{K})$ (C/m ²)	$C_p(298^\circ\text{K})$ (J/kg°K)	$\eta_{\max}$ (%)	$P_s(T_c)$ (C/m ²)	$C_p(T_c)$ (J/kg°K)	$\eta_{\min}$ (%)
LiTaO_3	891	7.45	0.71	0.50	430	1.40	0.36(723)	430(300)	0.71
LiNbO_3	1483	4.64	0.91	0.71	640	3.80	0.67(723)	640(300)	3.42
BaTiO_3	403	6.02	0.67	0.26	418	0.45	0.19	668	0.14
KNbO_3	691	4.59	0.47	0.30	740	0.31	0.26	740	0.23
$\text{K}(\text{Nb}_{0.94}\text{Ta}_{0.06})\text{O}_3$	656	4.29	0.54				0.18	792(298)	0.12
$\text{K}(\text{Nb}_{0.82}\text{Ta}_{0.18})\text{O}_3$	591	4.29	0.61				0.05	724(298)	0.01
PbTiO_3	763	7.50	1.00	0.81 0.50	360 360	6.10 2.31			
PZT(95/5)	493	7.41	0.32	0.34	451	0.26	0.23	451(300)	0.12
PLZT(8/65/35)	383	7.41	0.02	0.34	451	0.03	0.20	451(300)	0.01
PSZT	450	7.41	0.40	0.34	451	0.35	0.20	451(300)	0.16
$\text{Ba}_2\text{NaNb}_5\text{O}_{15}$	833	5.65	0.57	0.40	403	1.00			
SBN(60/40)	351	5.20	0.32	0.34	397	0.45			
SBN(50/50)	398	5.20	0.08				0.11	397(300)	0.01
KDP	123	2.34	79.20	0.05 (100)	305	6.10	0.03	368(100) 3680	2.10 0.21
NaNO_2	436	2.15	17.00	0.08	1090	1.16	0.05	1511(403) 39300	0.34 0.01
TGS	322	1.69	30.60	0.03	971	0.36	0.02(318)	1883	0.05
Rochelle Salt	298	1.78	50.40	0.01	741	0.01			
$\text{Pb}_5\text{Ge}_3\text{O}_{11}$	451	8.05	11.30	0.05	836	0.08			

If a more realistic value of 0.5 c/m^2 were taken for PbTiO_3 (rather than 0.81 c/m^2), the efficiency would drop from 6.1% to 2.3%! Aside from PbTiO_3 , other perovskites studied, included BaTiO_3 , KNbO_3 , KTN, and PZT solid solutions. Their efficiencies were lower, mainly because of lower P_s values. In the tungsten bronze family, barium sodium niobate (BNN) and barium strontium niobate (BSN) appeared to be the most promising candidate materials.

High polarizations per se are not the only criteria for conversion efficiency. In several cases, materials compensate for low P_s with high β coefficients and low densities. Examples include KDP with an η_{max} of 6.1% and NaNO_2 with 1.2%. However, both materials exhibit high first-order Λ anomalies in specific heat at the transition temperature, and efficiencies could decrease by orders-of-magnitude. This is illustrated in column 3 of Table 1.

COMMENTS AND SUMMARY

Solid-state heat engines will probably be equipped with polycrystalline dielectric layers, since problems in single crystal growth are extremely difficult at the present time, e.g. for PbTiO_3 . For these and other practical reasons, experiments were concentrated on the best commercially available materials. One of these was PLZT, which could be hot-pressed into large diameter forms. Unfortunately, the dielectric transitions were too broad, giving low β values. Sharper transitions were found in the PZT 95/5 system. Additions of tin oxide gave PZST compositions with a wide range of transition temperatures, permittivity maxima, β coefficients, and field enforceable effects. For example, hysteresis measurements on one particular composition indicated a ferroelectric-antiferroelectric transition at 130°C that was field enforceable up to 150°C , that is, over a 20°C range of temperature. This field enforceable temperature differential was taken as an indicator of the temperature range of operation, and of all the materials tested by Power Conversion Technology, this gave the greatest electrocaloric response!

Estimates of conversion efficiency were less than those previously stated,¹⁻⁶ principally due to lower values of P_s in commercially available materials. The most promising materials were those in the PZST system where transition temperatures were adjustable, switching speeds fast enough, and electrocaloric cooling the largest measured to date.

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REFERENCES

1. J. E. Drummond, Proc. Intersoc. Eng. Conv. Eng. Conf. (IEEE), **10**, 569 (1975).
2. J. D. Childress, J. Appl. Phys. **33**, 1793 (1962).
3. E. Fatuzzo, H. Keiss, and R. Nitsche, J. Appl. Phys. **37**, 510 (1966).
4. J. A. Gonzalo, Ferroelec. **11**, 423 (1976).
5. S. B. Lang, Ferroelec. **11**, 519 (1976).
6. J. E. Drummond, Proc. Intersoc. Eng. Conf. **12**, 1238 (1977).
7. M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Oxford: Clarendon Press (1977)