

## Recent Development Trend of Piezoelectric Single Crystals: A Review

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This review paper introduces the recent worldwide research and development trend of piezoelectric single crystals (PSC).

Lead perovskite compounds, such as lead magnesium niobate titanate (PMNT) and lead zinc niobate titanate (PZNT), have been investigated for transducer applications during the last 10 years. These materials have a large piezoelectric constant  $d_{33} > 2,000$  pC/N with Curie temperature  $T_c$  of 140-175°C. However, higher  $T_c$  perovskite compounds have been attracting attention in the last couple of years. New PSC materials with  $T_c > 180^\circ\text{C}$  have been intensively studied around the world. Some promising material systems, namely, In or Sc-doped PMNT, lead ytterbium niobate titanate (PYbNT), BiScO<sub>3</sub>-PbTiO<sub>3</sub> and potassium niobate (KN) PSC, are introduced. These new materials and the corresponding manufacturing processes are also summarized.

Key words: single crystal, review, lead perovskite, relaxors, piezoelectric.

### 1. INTRODUCTION

The potential piezoelectric properties of the perovskite (ABO<sub>3</sub>) structure of  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  (PZT) ceramics near the morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases were first clarified by Jaffe et al. in 1955[1]. After the discovery of PZT, numerous  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$  and  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3\text{-PbTiO}_3$  relaxor materials similar to PZT and new kinds of PSC have been investigated.[2-124]. From 1960 to 1980, attention focused on the interesting intrinsic properties of these relaxors, such as dielectric relaxation, the origin of their huge dielectric constants, and structure ordering. However, in the last 10 years, the main focus of attention has been the potential industrial applications of these relaxors.

The purpose of this article is to review the work carried out on  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3\text{-PbTiO}_3$  piezoelectric single crystal materials and their applications over the last 10 years. Recently, PSC have attracted great interest because their properties are far superior to those of conventional PZT ceramics. The present situation and future prospects regarding these PSC materials are also introduced. In addition, new material systems and their manufacturing processes are summarized

### 2. LEAD-BASED RELAXOR MATERIALS

#### 2.1 Relaxor Materials

Table I shows the Curie temperature  $T_c$ , maximum dielectric constant (K), crystal structure, ferroelectric (F) or antiferroelectric (AF) phase,  $\text{PbTiO}_3$  mol (%) at the MPB, and  $T_c$  at the MPB for various relaxor materials, along with their abbreviations. Figure 1 shows the MPB (I) in PZT and the MPB (II) in  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3\text{-PbTiO}_3$  and the MPB (III) in  $\text{Pb}(\text{B}'\text{B}'')\text{O}_3\text{-PZT}$ . The locations of the MPB (II) and (III) vary when different B' or B'' ions are selected as shown in Fig. 1. As regards practical piezoelectric applications, little attention was paid to MPB (II) and (III) compositions until 1980, due to the poor piezoelectric properties of the ceramics, notably their low electromechanical

coupling factors compared to those of PZT ceramics, and the high cost of the raw materials. Initially, lead magnesium niobate,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN), and lead zinc niobate,  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN), were considered to be the two best relaxors. Accordingly, they were the principal objects of research and used in many applications..

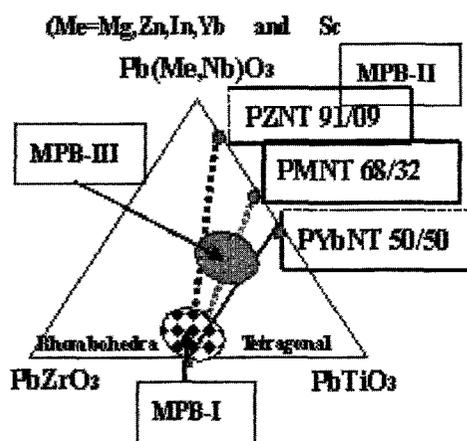


Figure 1 Location of MPB-I,II and III of relaxor-PT system.

#### 2.2 Importance of phase diagrams

This section reviews some basic studies of high-temperature phase diagrams of several relaxor materials. An accurate phase diagram is essential for growing single crystals of high quality and large size within a limited time frame. The first high-temperature phase diagram of the PMN and PbO systems was reported by Ye et al. [10]. Recently, based on the thermal analyses by TG/DAT, a complete pseudo-binary phase diagram between PZNT91/9 and PbO has been established [68]. The phase diagram and the thermodynamic data provide valuable guidance for the growth of

Table I Relaxor materials, high Tc materials and their MPBs with lead titanate

Relaxor Materials	Abbrev.	Tc K (°C)	$\epsilon_{max}$	Structure	Ferro.	Ti @ MPB (mol%)	Tc@MPB K (°C)
$Pb(B^{2+}_{1/3}B^{5+}_{2/3})O_3$							
$Pb(Cd_{1/3}Nb_{2/3})O_3$	PCdN	273 (0)	8,000	PC	F	28	653 (380)
$Pb(Zn_{1/3}Nb_{2/3})O_3$	PZN	413 (140)	22,000	R	F	9-10	448 (175)
$Pb(Mg_{1/3}Nb_{2/3})O_3$	PMN	263 (-10)	18,000	PC	F	32-34	428 (155)
$Pb(Ni_{1/3}Nb_{2/3})O_3$	PNN	153 (-120)	4,000	PC	F	30-35	403 (130)
$Pb(Mn_{1/3}Nb_{2/3})O_3$	PMnN	153 (-120)	4,000	PC	F	30-35	403 (130)
$Pb(Co_{1/3}Nb_{2/3})O_3$	PCoN	175 (-98)	6,000	M	F	33	523 (250)
$Pb(Mg_{1/3}Ta_{2/3})O_3$	PMgT	175 (-98)	7,000	PC	F	30?	373 (100)
$Pb(B^{3+}_{1/2}B^{5+}_{1/2})O_3$							
$Pb(Yb_{1/2}Nb_{1/2})O_3$	PYbN	553 (280)	150	M	AF	50	633 (360)
$Pb(In_{1/2}Nb_{1/2})O_3$	PIN	363 (90)	550	M	F	37	593 (320)
$Pb(Sc_{1/2}Nb_{1/2})O_3$	PSN	363 (90)	38,000	R	F	42	533 (260)
$Pb(Fe_{1/2}Nb_{1/2})O_3$	PFN	385 (112)	12,000	R	F	7?	413 (140)
$Pb(Sc_{1/2}Ta_{1/2})O_3$	PST	299 (26)	28,000	R	F	45	478 (205)
Others							
* $PbZrO_3$	PZ	513 (240)	3,000	O	AF	47	633 (360)
$(Pb,La)(Zr,Ti)O_3$	PLZT	<623 (<350)	30,000	R, T	F, AF	35-47	<623 (<350)
$BiScO_3$	BS	>673 (>350)	<1,000	R	F	64	723 (450)
$BiInO_3$	BIn	>973 (>700)	<1,000	R	F?	70	843 (570)
$(Na_{1/2}Bi_{1/2})TiO_3$	BNT	633 (360)	4,000	R	F	5BT	573(300)
$KNbO_3$	KN	708 (435)	7,000	R	F	50NaNbO3	<673 (<400)
$PbTiO_3$	PT	763 (490)	9,000	T	F		

C: Cubic, M: Monoclinic, O: Orthorhombic,  
 PC: Pseudocubic, PY: Pyrochlore, R: Rhombohedral, T: Tetragonal  
 AF: Antiferroelectrics, F: Ferroelectrics

Table II Comparison of several relaxor-PT single crystals and PZT5H ceramics for transducer applications.

Materials	Ti (mol%)	Tc (°C)	$K_{33}$	$k_{33}$ (%)	$k_{31}$ (%)	$d_{33}$ (pC/N)	$d_{31}$ (pC/N)	$g_{33}$ ( $\times 10^{-3}Vm/N$ )	Size (mm)
PZNT	5-10	150-175	4,000	95	81	2,400	-1,700	60	50
PMNT	30-35	135-155	4,500	93	61	2,500	-1,000	50	50
PSNT	38-43	240-260	2,000	(94*)	(80*)	(1,500)	(-1,000)	(>40)	<10
PINT	33-38	300-320	2,000	(85*)	(>50)	(1,000)	(-700)	(>40)	<15
PIMNT	30-35	180-250	3,100	90	60	2,200	-1,000	60	25
$BiScO_3$ -PT	64	450	2000	75	40	450	-	26	<10
$KNbO_3$		420	110	$kt=70$	(60*)	55	-	55	<50
PZT 5H**	40-47	210	3,200	75	40	700	-350	20	>100

(\*) Predicted value, \*\* Ceramics

large and high-quality PZNT PSC. A solution Bridgman process has been successfully developed to grow PZNT single crystals with various  $\text{TiO}_2$ -concentrations. This process has resulted in good quality PSC of large size (25-80mm in diameter and more than 1.0 kg in weight), suitable for medical echo and many other transducer applications[71,76,99].

### 2.3 Large size single crystal growth

The first large-size PSC growth was carried out by Bonner et al. in 1967 [5]. A PZNT PSC by flux growth for medical transducer applications was first reported by Kobayashi in 1997 [19]. However, in recent years, PSC growth has been performed by the solution Bridgman or Bridgman process. Using these processes, it is possible to control evaporation of  $\text{PbO}$  at high temperature during crystal growth. The PSC growth by the Bridgman process started at about the same time in Japan [26,27], the USA [37] and China [39,58]. The Bridgman process furnace has a steep vertical temperature gradient, more than  $20^\circ\text{C}/\text{cm}$ , at around solid/liquid interfaces determined by the phase diagram. Figure 2 shows the large PZNT PSC boule produced by the solution Bridgman process[76,112]. PMNT and PZNT PSC of almost the same size have been successfully grown in other organizations[108-111].

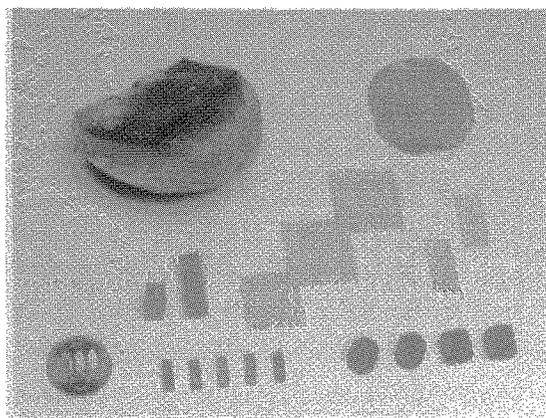


Figure 2 Large size PZNT PSC produced by the solution Bridgman process.(Courtesy of Kawatetsu Mining Co., Japan, see[112])

### 2.4 High Curie temperature PSC

One of the disadvantages of PZNT and PMNT PSC is that they have a low Curie temperature  $T_c$  and a low rhombohedral to tetragonal phase change temperature  $\text{Trt}$ , compared to those of PZT ceramics. Unlike PZT ceramics, PZNT and PMNT exhibit a phase change temperature  $\text{Trt}$  of around  $50$ - $120^\circ\text{C}$ . Although the  $\text{Trt}$  values shift depending on poling conditions, fairly large decreases of  $k_{33}$  and  $d_{33}$  are observed above the  $\text{Trt}$  [43,80]. Therefore, the operating temperature range of these PSC devices is practically limited by  $\text{Trt}$ , not by  $T_c$ . The  $T_c$ s and  $\text{Trt}$ s of PZNT94/6 to PZNT89/11 lie in the ranges of  $T_c=161$ - $178^\circ\text{C}$  and  $\text{Trt}=107$ - $47^\circ\text{C}$ , and those of PMNT70/30 to PMNT67/33 in the ranges of  $T_c=140$ - $155^\circ\text{C}$  and  $\text{Trt}=87$ - $47^\circ\text{C}$ . These  $\text{Trt}$  and  $T_c$ s are sufficiently high for naval or medical applications where the operating temperatures are

usually below  $60^\circ\text{C}$ . However, they are unsuitable for high-temperature applications such as actuators for outdoor use. Therefore, new material systems with  $T_c > 180^\circ\text{C}$  and  $\text{Trt} > 100^\circ\text{C}$  are required for high-temperature applications. Using the binary system of  $x\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $y\text{PbTiO}_3$  (PINT 100x/100y) [28,46,61] and the ternary system of  $x\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $y\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $z\text{PbTiO}_3$  (PSMNT 100x/100y/100z), attempts have been made to grow PSC of sufficient size. Yasuda et al. reported that PINT single crystals of fairly good quality, more than  $10 \times 10 \times 3\text{mm}$  in size, were obtained by the flux method [44,59]. The PINT single crystal shows a  $T_c$  of  $260^\circ\text{C}$ , which is  $80^\circ\text{C}$  higher than that of the PZNT 91/9 single crystal. A  $\text{Trt}$  is observed near  $100$ - $150^\circ\text{C}$ . The PSMNT single crystal shows a peak dielectric constant maximum at  $T_c=200^\circ\text{C}$  at 1 kHz, which is  $50^\circ\text{C}$  higher than that of the PMNT 67/33 single crystal. A small peak of dielectric constant is observed near  $120^\circ\text{C}$ , which is considered to be a transition point ( $\text{Trt}$ ) from rhombohedral to tetragonal phase [61]. The PINT shows excellent temperature dependence of piezoelectric properties [61].

Recently, Hosono et al. reported piezoelectric properties of  $x\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ - $y\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $z\text{PbTiO}_3$  (PIMNT 100x/100y/100z) PSC[83]. Figure 3 shows the dielectric constants before poling of the PIMNT 16/51/33 PSC of different boule positions. Low  $T_c$  ( $T_c=181^\circ\text{C}$ ) of the wafer was obtained near the nucleation area, whereas high  $T_c$  ( $T_c=196^\circ\text{C}$ ) of the wafer was obtained at the top of the boule. These characteristics are almost the same as those of the PMNT PSC grown by the Bridgman process. The variation is caused by  $\text{TiO}_2$  composition difference between and within the PIMNT PSC wafers. A large dielectric constant maximum, ranging from 38,400 to 41,800 was observed. A low loss of less than 1.5% after poling was seen in wafer #-1, whereas a slightly larger loss of 1.5% was seen at the end part. A noticeably large  $d_{33}=1,950\text{ pC/N}$ , which is about 4 times larger than that of the same ceramics composition, was obtained in the center portion of wafer #-8. The  $T_c$  of the wafer is  $191^\circ\text{C}$ , which is  $40^\circ\text{C}$  higher than that of the PMNT 68/32. The sliver mode electromechanical coupling factor  $k'_{33}$  was measured with a 0.36mm thick  $\times$  0.17mm wide  $\times$  9mm long specimen. The width/thickness ratio is 0.47 which is sufficient to obtain a clean spectrum for the thickness mode vibration. A large  $k'_{33} > 80\%$ , which is almost the same as for the PMNT 68/32, was obtained in wafers #-1 and #-8. The PIMNT PSC have not only a large  $d_{33}=2,000\text{ pC/N}$ , but also high  $T_c$  of  $170$ - $200^\circ\text{C}$ . PIMNT PSC produced by the Bridgman process and TSSG process were also reported[97,98]. The PIMNT PSC are considered to be a good candidate of medical array transducers due to their well balanced electrical properties [83,96,97]. Table II summarizes various important relaxor-PT PSC and other PSC properties and compares them with those of PZT5H ceramics.

### 2.5 New PSC manufacturing process

The Bridgman process and TSSG process are well established PSC growth processes[71]. However, these processes have several shortcomings, such as

Pt crucible cost and composition homogeneity. In order to solve these shortcomings, a new approach has been studied. Solid state crystal growth (SSCG) and templated crystal growth (TCG) processes have many advantages. The first SSCG process for lead-relaxor materials was studied by Yamashita et al. in early 1998[49]. At almost the same period, many researchers also tried to make relaxor PSC by these process [50,74,81,89,90,102,104,109]. Since these processes have many advantages compared to the conventional PSC process, they are expected to lead to the reduction of the cost of relaxor PSC for mass-production in the near future..

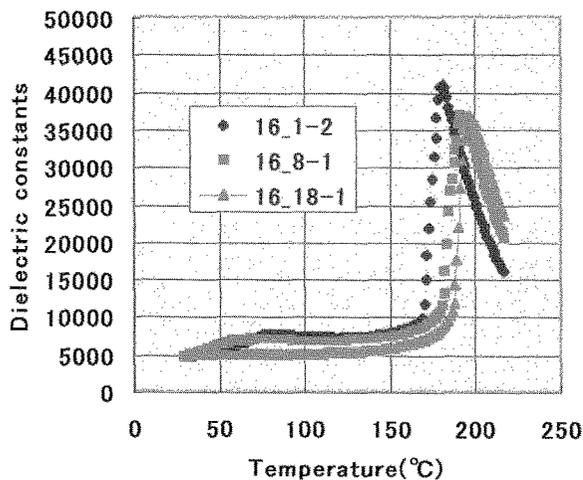


Figure 3. Dielectric properties of PIMNT 16/51/33 PSC of different wafer position for in the boule (Before poling)

### 3. APPLICATIONS

Medical echo diagnostic ultrasound systems use ultrasonic array transducers for their applications. Frequencies used for these applications are 2-20 MHz. The typical cardiac transducer operates at a center frequency of 2-4 MHz and makes use of a piezoelectric material plate with a size of 15 x 25 mm. Recently, medical echo ultrasound has been greatly improved. The color Doppler technique and tissue harmonic imaging are frequently used for functional diagnosis as well as for ultrasonic tomography (B mode). However, clearer images are required for early and reliable diagnosis of human organs with small tumors. This requires a wider bandwidth of probes as well as improved sensitivity. The key to achieve this is the performance of the piezoelectric material which transmits and receives the echo ultrasound. High dielectric constant type PZT5H ceramics have been mostly used for this application in recent decades. However, recent research has focused on obtaining greater sensitivity and broader bandwidth, and new transducers such as piezoelectric composites have been studied. Single crystals of PZNT91/9 and PMNT67/33 have a large  $d_{33}$  ( $>2,000$  pC/N) and  $k_{33}$  ( $>92\%$ ),  $k_{33}^2$  ( $>80\%$ ) and  $g_{33}$  ( $>60 \times 10^{-3}$  Vm/N), values far larger than those obtained for any PZT ceramic specimens. This is one reason that intensive research on medical transducers has been

conducted in various parts of the world during the last 10 years. After the initial reports and presentations by Toshiba in the early 1990s [12,15,18,19,23,27,31,34,35,40], several organizations in the USA, entered the field [16,20-22,24,29,30,33,36,47,48]. Saitoh et al. reported the first images of B-mode and Doppler-mode obtained by using PZNT91/09 PSC for cardiac transducers operating at 3.5 MHz with 96 channels [34]. The echo amplitude of the PZNT probe is about 6 dB higher than that of the PZT probe, and the frictional bandwidth is 30% wider. This means that both the penetration and the resolution of the PZNT probe are superior to those of conventional PZT probes. Large coupling factor  $k_{33}^2$  ( $>82\%$ ), dielectric constant after poling ( $K > 3,000$ ) and low acoustic impedance  $Z_{33} < 24$  ( $\times 10^6$  kg/m<sup>2</sup>s) make PZNT 91/9 single crystals an excellent transducer material for medical diagnostic applications. At present, the size of PZNT and PMNT PSC is sufficient for various applications. However, the quality and uniformity of these crystals within and between the wafers, as well as among lots and among manufacturers, are still insufficient[82]. Although it is usually easy to grow PZNT and PMNT PSC in [111] or [110] directions, it is very difficult to grow them in [001] direction[57,82]. Since [001] wafers are used for medical transducers, there is always some TiO<sub>2</sub> distribution within wafers[58]. This is one of the causes of large scattering of  $k_{33}$ ,  $d_{33}$  and dielectric constant within wafer. In addition, the manufacture of high-frequency, i.e. more than 7 MHz, PSC transducers that requires thin thickness plate (less than 150 microns), is very difficult because of the low-frequency constant and low mechanical strength of PSC. The present cost of PSC wafers is more than 10 times that of PZT ceramics. Other drawbacks are temperature instability, mechanical properties, chipping by dicing, matching layers/electrode/PSC bonding strengths, low clamped dielectric constant, low  $E_c$ , depoling and low production yield, etc. So, at present, although PSC have properties which are very attractive compared to those of PZT ceramics, the supply of PSC medical array transducers is limited.

Figure 4 shows 3 MHz cardiac PMNT PSC transducer. The properties are superior to those of PZT transducer as shown in Fig. 5.

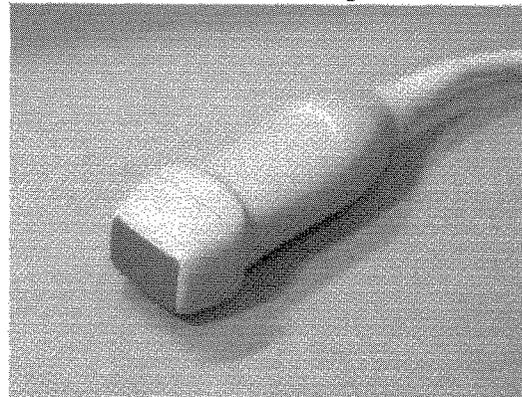


Figure 4 3MHz PMNT PSC transducer (Courtesy of Humanscan Co., Korea, see[111])

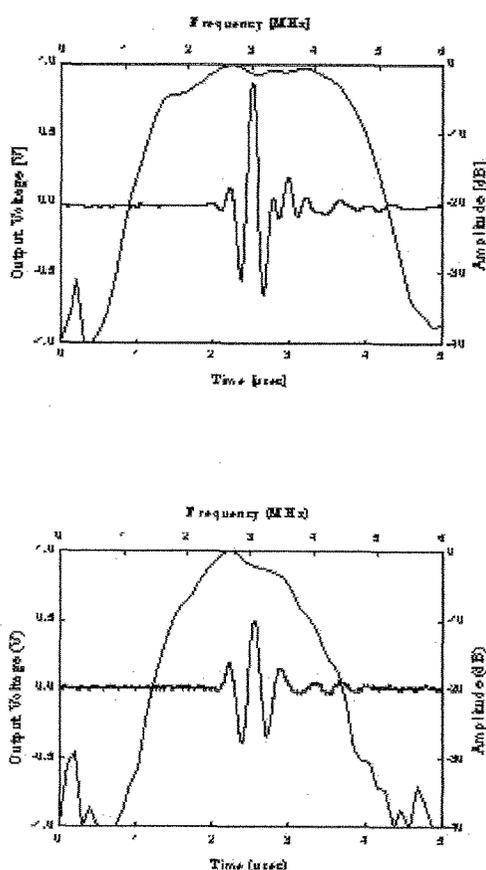


Figure 5 Two way spectrum of (Top) PMNT PSC transducer with  $-6\text{dB RBW}=100\%$  and (Bottom) PZT transducer with  $-6\text{dB RBW}=65\%$ . (Courtesy of Humanscan Co., Korea, see[111])

#### 4. OTHER PSC MATERIALS

##### 4.1 Bismuth perovskite compounds,

Bismuth perovskite of  $\text{BiScO}_3\text{-PbTiO}_3$  PSC was reported by Zhang[86,87,88]. The material system has a high  $T_c$  of  $450^\circ\text{C}$  with a large  $d_{33}>450$  pC/N, which is suitable for high-temperature applications above  $300^\circ\text{C}$ .

##### 4.2 Potassium niobate $\text{KNbO}_3$

Potassium niobate ( $\text{KNbO}_3$ , KN) crystals undergo a sequence of phase transitions from the cubic phase to tetragonal, orthorhombic, and rhombohedral phases with decreasing temperature, i.e. at  $435^\circ\text{C}$ ,  $225^\circ\text{C}$ , and  $-10^\circ\text{C}$ , respectively. The structural phase transformation sequence in potassium niobate is analogous to that of  $\text{BaTiO}_3$ . The orthorhombic single crystal of KN has a pseudocubic perovskite structure. Potassium niobate is known to melt incongruently at  $1039^\circ\text{C}$  and single crystals are usually grown from a  $\text{K}_2\text{CO}_3\text{-Nb}_2\text{O}_5$  melt with excess  $\text{K}_2\text{CO}_3$  acting as a flux by the Kyropoulos technique or the TSSG (top-seeded solution growth) technique. Figure 6 shows a photograph of a KN single crystal with dimensions of about  $40\times 40\times 25$  mm<sup>3</sup>, which was produced by Asahi Techno Glass Co., Japan. Similar PSC are also manufactured by several organizations. Potassium niobate PSC had not received much attention as a

piezoelectric material until very high coupling factors both for surface acoustic waves [113,116] and bulk acoustic waves [114,117] were reported. Electromechanical coupling factors thickness mode  $kt=70\%$  and piezoelectric charge constant  $g_{33}=55(\times 10^{-3}\text{V/mN})$  of KN PSC with special cutting angles are very attractive for device engineers. New applications for KN PSC have been proposed [118,119,121,122,123].



Fig.6 KN PSC produced by Kyropoulos process (Courtesy of Asahi Techo Glass Co., Japan, see[124])

#### 5. CONCLUSION

(1) Sufficiently large PZNT and PMNT piezoelectric single crystals (PSC), i.e. 25-80mm in diameter, for various applications such as medical transducers, actuators, sonar and hydrophones, are available

(2) Process capabilities, such as polishing, electroding, dicing, lead-attaching and the assembling of 2-7.5MHz medical cardiac PSC transducers, are almost established.

High quality of images on screens of medical echo systems has been confirmed by several echo equipment manufacturers.

(3) Quality, uniformity level between and within wafers, lot to lot and among manufacturers of PSC made by the (solution) Bridgman process are still inferior to those of PZT ceramics.

(4) Design and manufacture of high-frequency PSC array transducers, i.e. higher than 8MHz, is very difficult due to the low frequency constant and mechanical strength of PSC.

(5) New high  $T_c$  PSC of In-doped PMNT,  $\text{BiScO}_3\text{-PT}$ , and KN would be very promising for high-temperature applications if PSC of sufficient size and quality were grown.

(6) Some other drawbacks of PSC array transducers have been pointed out. So, at present, PSC have yet to win acceptance in the mass production of medical array transducers except at a few organizations. Nevertheless, it is quite possible that PSC may become the predominant materials for sophisticated, performance-oriented piezoelectric products in the near future.

(7) Regarding future tasks, research on methods of

evaluating PSC wafer quality and uniformity using non-destructive processes is urgently required[99]. Improvement in the uniformity of capacitance,  $c/m$  coupling factors  $k_{33}$  and piezoelectric constant  $d_{33}$  within and between wafers is also a major task for crystal growers. Detailed basic research to determine the mechanism accounting for the scattering of electrical properties should be studied from the viewpoints of composition, domain structure and defect chemistry. Finally, research on new PSC materials and PSC growth technology to solve all the present problems is essential. From the viewpoint of applications, a new dicing process which prevents cracking of PSC is also necessary in order to make fine pitch array transducers.

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#### REFERENCES

- B. Jaffe, *J. Res. Nat. Bur. Stand.*, **55**, 239-48 (1955).
- G.A. Smolenskii, V.A. Isupov, A.L. Agranovskaya, *Soviet Phys. Solid State*, **1**, 150-51 (1958).
- S. Fusimi and T. Ikeda, *Jpn. J. Appl. Phys.*, **3**, Short Note, 171-72 (1964).
- H. Ouchi, K. Nagano, S. Hayakawa, *J. Am. Ceram. Soc.*, **48**, No.12, 630-35 (1965).
- W.A. Bonner, and L.G. Van Uitert, *Mat. Res. Bull.*, **1**, 2, 131-134 (1967).
- Y. Yokomizo, T. Takahashi, and S. Nomura, *Jpn. J. Appl. Phys.*, **28**, 1278-84 (1970).
- K. Uchino, and S. Nomura, *J. Appl. Phys.*, **51**, No.2, 1142-45 (1980).
- J. Kuwata, K. Uchino, and S. Nomura, *Jpn. J. Appl. Phys.*, **21**, No.9, 1298-302 (1982).
- T.R. Shrout, Z.P. Chang, N. Kim and S. Markgraf, *Ferroelectric Letters*, **12**, 63-69 (1990).
- Z.G. Ye, T. Tissot and H. Schmid, *Mater. Res. Bull.*, **25**, 739-48 (1990).
- Y. Yamashita, *Jpn. J. Appl. Phys.*, **33**, 4652-56 (1994).
- S. Saitoh, M. Izumi, S. Shimanuki, S. Hashimoto, and Y. Yamashita, Ultrasonic probe, U.S. Patent 5,295,487, USA, Mar. 22, 1994.
- T. Yamamoto and S. Ohashi, *Jpn. J. Appl. Phys.*, **34**, 5349-53 (1995).
- H. Lim, H.J. Kim, W.K. Choo, *Jpn. J. Appl. Phys.*, **34**, 5449-52 (1995).
- Y. Yamashita and N. Ichinose, Proc. of the *IEEE ISAF* 71-77 (1996).
- S. Park and T. Shrout, *Proc. of IEEE ISAF*, 935-42 (1996).
- S.W. Choi, J.M. Jung, and A.S. Bhalla, *Ferroelectrics*, **189**, 27-38 (1996).
- Y. Yamashita, and K. Harada, *Jpn. J. Appl. Phys.*, **36**, 9B, 6039-42 (1997).
- T. Kobayashi, S. Shimanuki, S. Saitoh and Y. Yamashita, *Jpn. J. Appl. Phys.*, **36**, No. 9B, 6035-38 (1997).
- S. Park and T. Shrout, *J. Appl. Phys.*, **82**, 1804-11 (1997).
- S. Park, P. Lopath, K. Shung, and T. Shrout, *Proc. SPIE*, **3037**, 140-47 (1997).
- P. Lopath, K. Shung, S. Park and T. Shrout, *Proc. SPIE*, **3037**, 170-74 (1997).
- S. Saitoh, T. Kobayashi, S. Shimanuki and Y. Yamashita, *Proc. SPIE*, **3037**, 22-29 (1997).
- S. Park and T. Shrout, *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, **44**, No.5, 1140-47 (1997).
- K. Fujishiro, R. Vlokh, Y. Uesu, Y. Yamada, J.M. Kiat, B. Dkhil and Y. Yamashita, *Jpn. J. Appl. Phys.*, **37**, 5246-48 (1998).
- S. Shimanuki, S. Saitoh and Y. Yamashita, *Jpn. J. Appl. Phys.*, **37**, 3382-85 (1998).
- K. Harada, S. Shimanuki, T. Kobayashi, S. Saitoh, and Y. Yamashita, *J. Am. Ceram. Soc.*, **81**, 2585-2788 (1998).
- T. Shrout, S.E. Park, P. Lopath, R. Meyer, T. Ritter and K. Shung, *Proc. SPIE* **3341**, 174-83 (1998).
- P. Lopath, K. Shung, S. Park and T. Shrout, *Proc. SPIE* **3341**, 242-48 (1998).
- T. A. Ritter, K. Shung, X. Geng, and T. Shrout, *Proc. SPIE* **3341**, 249-61 (1998).
- S. Saitoh, T. Kobayashi, K. Harada, S. Shimanuki, and Y. Yamashita, *Proc. SPIE* **3341**, 264-71 (1998).
- K. Yanagisawa and J. C. Rendon-Angeles, *J. Mater. Sci. Lett.* **17**, 2105-07 (1998).
- S.E. Park, and T.R. Shrout, High strain actuator using ferroelectric single crystal, U.S. Patent, 5,804,907, USA, Sep., 8, 1998.
- S. Saitoh, T. Kobayashi, S. Shimanuki, and Y. Yamashita, *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, **45**, No.4, 1071-76 (1998).
- S. T. Saitoh, T. Kobayashi, K. Harada, S. Shimanuki and Y. Yamashita, *Proc. SPIE* **3664**, 147-54 (1998).
- X. Geng, T.A. Ritter and S. E. Park, 1998 Proc. *IEEE Ultrason. Symp.*, 571-74 (1998).
- S.G. Lee, R.G. Monteiro and R.S. Feigelson, *Appl. Phys. Lett.*, **74**, 1030-32 (1999).
- Z.-G. Ye, M. Dong and L. Zhang, *Ferroelectrics*, **229**, 223-32 (1999).
- H. Luo, G. Xu, P. Wang, and Z. Yin, *Ferroelectrics*, **231**, 97-102 (1999).
- S. Saitoh, T. Takeuchi, T. Kobayashi, K. Harada, S. Shimanuki, and Y. Yamashita, *Jpn. J. Appl. Phys.*, **38**, No. 5B, 3380-84 (1999).
- Y. Hosono, K. Harada, S. Saitoh, and Y. Yamashita, *Jpn. J. Appl. Phys.*, **38**, 9B, 5512-15 (1999).
- J. Yin, B. Jiang and W. Cao, *Proc. SPIE* **3664**, 239-46 (1999).
- G. Robert, D. Damjanovic and N. Setter, *Ferroelectrics*, **224**, 97-104 (1999).
- Y. Yasuda, H. Ohwa, K. Ito, M. Iwata, and Y. Ishibashi, *Ferroelectrics*, **230**, pp. 115-120 (1999).
- W-G. Luo, A-L. Ding, H. Luo and Z. W. Yin, 1999 Proc. *IEEE Ultrason. Symp.*, 1009-12

- (1999).
46. S. Wada, S. Suzuki, T.Noma, T.Suzuki, M. Osada, M.Kakihana, S.E.Park, L.E.Cross and T.R.ShROUT, *Jpn. J. Appl. Phys.* **38**,5505-09 (1999).
  47. T. R. Gururaja, R. K. Panda J. Chen and H. Beck, 1999 Proc. *IEEE Ultrason. Symp.*, 969-72 (1999).
  48. Park, S.E., ShROUT, T. R., and Lopath, P.D., Relaxor ferroelectric single crystals for ultrasonic transducers, U.S.Patent, 5,998,910, USA, Dec.7, 1999.
  49. Y.Yamashita, S. Shimanuki, K.Harada, T.Kobayashi, S.Saitoh and M.Kawachi, Ultrasonic probe, U.S. Patent 6,020,675, USA, Feb.01, 2000. SSCG
  50. M.P. Harmer, M.H. Chan, H.Y.Lee, M.A. Scotch, T.Li, F. Meschke, A.Khan, Method for growing single crystals from polycrystalline precursors, U.S. Patent 6,048,394, USA, Apr. 11, 2000.
  51. S.F. Lu, Z.Y. Cheng, S.E. Park, S.F. Liu and Q.M. Zhang, *Jpn. J. Appl. Phys.* **39**,141-45 (2000).
  52. J. Zipparo, and C. G. Oakley, Proc. of *IEEE ISAF*, 111-14 (2000).
  53. J.F. Tressler, and T.R., Howarth, Proc. of *IEEE ISAF*, 561-64 (2000).
  54. S. Wan and C.S. Lynch, Proc. of *IEEE ISAF*, 347-49 (2000).
  55. J.M. Powers, M.B. Moffett and F. Nussbaum, Proc. of *IEEE ISAF*, 351-54 (2000).
  56. P.A. Wlodkowski, K. Deng, M. Kahn and M.T. F. Chase, Proc. of *IEEE ISAF*, 565-67 (2000).
  57. Q.R. Yin, J.W. Fang, H.S. Luo and G.R. Li, Proc. of *IEEE ISAF*, 569-72 (2000).
  58. H. Luo, G. Xu, H. Xu, P. Wang and Z. Yin, *Jpn. J. Appl. Phys.*, **39**, 9B, 5581-85 (2000).
  59. Y. Yasuda, H. Ohwa, M. Kume and Y. Yamashita, *Jpn. J. Appl. Phys.*, **39**, Part 2, No.2A, L66-68 (2000).
  60. Z.-G. Ye and M. Dong, *J. Appl. Phys.*, **87**, 2312-19 (2000).
  61. Y. Hosono, K. Harada, Y. Yamashita, M. Dong and Z.-G. Ye, *Jpn. J. Appl. Phys.*, **39**, 9B, 5589-92 (2000).
  62. C.G. Oakley and M.J. Zipparo, Proc. of *IEEE Ultrasonic Symposium*, 1157-67 (2000).
  63. T. Ritter, X. Geng and K. K. Shung, *IEEE Trans. Ultrason. Ferroelect. Freq. Contr.*, **47**, 792-800 (2000).
  64. V. Bornand, S. Trolier-McKinstry, K. Takemura, and C.A. Randall, *J. Appl. Phys.*, **87**, 3965-72 (2000).
  65. K.Watari, B.Brahmaroutu, G.L.Messing, S.T.McKinstry, and S.C. Cheng, *J. Mater. Res.*, **15**,846-49(2000). TGG
  66. Y. Yasuda, H. Ohwa, H. Hasegawa, M. Kume, Y. Hosono, Y. Yamashita, S. Ishino, H. Terauchi, M. Iwata and Y. Ishibashi, *Jpn. J. Appl. Phys.*, **40**, No.9B, 5664-67 (2001).
  67. Y. Hosono, K. Harada and Y. Yamashita, *Jpn. J. Appl. Phys.*, **40**, No.9B, 5722-26 (2001).
  68. M. Dong and Z.-G. Ye, *Jpn. J. Appl. Phys.*, **40**, 4604-10 (2001).
  69. K. Harada, Y. Hosono, Y. Yamashita and K. Miwa, *J. Cryst. Growth*, **229**, 294-98 (2001).
  70. W. Chen and Z.-G. Ye, *J. Crystal Growth*, **233**, 503-11 (2001).
  71. K. Harada, Y. Hosono, Y. Yamashita and K. Miwa, *J. Cryst. Growth*, **229**, 294-98 (2001).
  72. Y. Yamashita, T. Kobayashi, S. Saitoh, K. Harada and S. Shimanuki, Method of manufacturing ultrasonic probe and ultrasonic diagnostic apparatus, U.S. Patent 6,238,481 B1, USA, May 29, 2001.
  73. E.F.Alberta, A.S.Bhalla and R. Guo, *Ferroelectrics Review*, **3**, [1-4], 1-328 (2001)
  74. H. Y. Lee, J.S. Kim, J.H.Lee, T.M. Hur, D.Y. Kim, N.M. Hwang, B.K.Lee, K. B. Chung, S.Y. Kang, J.L. Suk, Method for single crystal growth of barium titanate and barium titanate solid solution U.S. Patent 6,482,259, USA, Nov. 19, 2002.
  75. S.G.Lee, S.M. Rhim, M.C.Kim, Ferroelectric single crystal wafer and process for the preparation thereof, U.S. Patent 6,491,889, USA, Dec.10, 2002.
  76. M. Matsushita, Y. Tachi, K. Echizenya, *J. Cryst. Growth*, **237-239**,853-57 (2002).
  77. T. Ogawa, Y. Yamauchi, Y. Numamoto, M. Matsushita and Y. Tachi, *Jpn. J. Appl. Phys.* **41**, L55-58 (2002).
  78. Y. Hosono, K. Harada, T. Kobayashi, K. Itsumi, M. Izumi, Y. Yamashita and N. Ichinose, *Jpn. J. Appl. Phys.*, **41**, 3808-11 (2002).
  79. T.Karaki, M. Nakamoto, and M.Adachi, *Jpn. J. Appl. Phys.*, **41**, 6997-99 (2002).
  80. Y. Hosono, K. Harada, T. Kobayashi, K. Itsumi, M. Izumi, Y. Yamashita and N. Ichinose, *Jpn. J. Appl. Phys.*, **41**, 7084-88 (2002).
  81. T. R. ShROUT, R. Eitel and C. A. Randall, "Piezoelectric Materials in Devices", Ed. by N. Setter ,EPFL Swiss Federal Institute of Technology, Lausanne 1015, Switzerland, ISBN-2-9700346-0-3, (2002),pp.413-54.
  82. Y.Yamashita, Y.Hosono and Z.G. Ye, "Piezoelectric Materials in Devices", Ed. by N. Setter ,EPFL Swiss Federal Institute of Technology, Lausanne 1015, Switzerland, ISBN-2-9700346-0-3, (2002),pp.455-66.
  83. Y. Hosono, Y. Yamashita, H. Sakamoto and N. Ichinose, *Jpn. J. Appl. Phys.*, **41**, L1240-L42 (2002).
  84. S.M. Rhim, H. Jung, S.Kim and S.G. Lee, Proc. of *IEEE Ultrasonic Symposium*, 1115-19 (2002).
  85. Y. Yamashita, Y. Hosono, K. Harada and N. Yasuda, *IEEE Trans. Ultrason. Ferroelect. & Freq. Control*. **49**, 184 (2002).
  86. S. J. Zhang, S. Rhee, C. A. Randall and T. R. ShROUT: *Jpn. J. Appl. Phys.* **41**, 722 (2002).
  87. S. J. Zhang, L. Lebrun, S. Rhee, C. A. Randall and T. R. ShROUT, *Appl. Phys. Lett.* **81**, 892 (2002).
  88. S. J. Zhang, P. W. Rehrig, C. A. Randall and T. R. ShROUT, *J. Cryst. Growth*, **234**, 415 (2002).
  89. Q. Q. Zhang, Q. F. Zhou and S. Trolier-McKinstry, *Appl. Phys. Lett.*, **80**, 3370 (2002).

90. T. Yoshimura and S. Trolier-McKinstry, *J. Appl. Phys.*, **92**, 3979 (2002).
91. R. Eitel, C. A. Randall, T. R. Shrout and S. E. Park, *Jpn. J. Appl. Phys.*, **41**, 2099 (2002).
92. S. J. Zhang, L. Lebrun, S. Rhee, R. E. Eitel, C. A. Randall and T. R. Shrout, *J. Cryst. Growth*, **236**, 210 (2002).
93. S. Wada, H. Kakemoto, T. Tsurumi, S. E. Park, L. E. Cross and T. R. Shrout, *Trans. Mater. Res. Soc. Jpn.*, **27**, 281 (2002).
94. S. G. Lee, J. Y. Kim, H. J. Kim, Surface Acoustic Wave Filter Using Novel Piezoelectric Single Crystal Substrate, U.S. Patent 6,545,387, USA, Aug. 08, 2003.
95. Y. Hosono, Y. Yamashita, H. Sakamoto and N. Ichinose, *J. Appl. Phys.*, **42**, 535-38 (2003).
96. Y. Hosono, Y. Yamashita, H. Sakamoto and N. Ichinose, *Appl. Phys.*, **42**, 5681-86 (2003).
97. Y. Hosono, Y. Yamashita, H. Sakamoto and N. Ichinose, *Jpn. J. Appl. Phys.*, **42**, 6062-67 (2003).
98. T. Karaki, M. Nakamoto, Y. Sumiyoshi, M. Adachi, Y. Hosono and Y. Yamashita, *Jpn. J. Appl. Phys.*, **42**, 6059-61 (2003).
99. L. C. Lim, F. J. Kumar and A. Amin, *J. Appl. Phys.*, **93**, 3671 (2003).
100. F. J. Kumar, L. C. Lim, S. P. Lim, and K. H. Lee, *IEEE Trans. Ultrason., ferroelect., Freq. Contr.*, **50**, 203-09 (2003).
101. Z.-G. Ye, Y. H. Bing, J. Gao, A. A. Bokov, P. Stephens, B. Noheda and G. Shirane, *Phys. Rev. B* **67**, 104-08 (2003).
102. Q. F. Zhou, Q. Q. Zhang, T. Yoshimura and S. Trolier-McKinstry: *Appl. Phys. Lett.* **82**, 4767 (2003).
103. S. J. Zhang, D. Y. Jeong, Q. M. Zhang and T. R. Shrout: *J. Cryst. Growth*, **247**, 131 (2003).
104. E. M. Sabolsky, S. T. McKinstry and G. L. Messing, *J. Appl. Phys.*, **93**, (7), 4072-80 (2003).
105. H. Dammak, A. É. Renault, P. Gaucher, M. P. Thi and G. Calvarin, *Jpn. J. Appl. Phys.* **42**, 6477-82 (2003).
106. S. Zhang, C. A. Randall and T. R. Shrout, *Jpn. J. Appl. Phys.* **42**, L1152-54 (2003).
107. <http://www.ibule.com/>
108. <http://www.hcmat.com/>
109. <http://www.ceracomp.com/>
110. <http://trsceramics.com>
111. <http://ibulehumanscan.koreasme.com>
112. <http://www.kawako.kawatetsu.ne.jp>
113. K. Yamanouchi, H. Odagawa, T. Kojima and T. Matsumura, *Electron. Lett.* **33**, 193-94 (1997).
114. K. Nakamura and M. Oshiki, *Appl. Phys. Lett.* **71**, 3203-05 (1997).
115. H. Odagawa and K. Yamanouchi, *Jpn. J. Appl. Phys.* **37**, 2929-32 (1998).
116. K. Yamanouchi, H. Odagawa, K. Morozumi and Y. Cho, *Jpn. J. Appl. Phys.* **37**, 2933-35 (1998).
117. K. Nakamura and Y. Kawamura, *IEEE Trans. Ultrason. Ferroelect. Freq. Contr.* **47**, 750-55 (2000).
118. N. M. Kari, T. A. Ritter, S. E. Park, T. R. Shrout and K. K. Shung, *Proc. 2000 IEEE Ultrason. Symp.*, 1065-1068 (2000).
119. H. Adachi, K. Wakabayashi, M. Nishio, H. Ogawa, and T. Kamakura, *Jpn. J. Appl. Phys.* **40**, 5698-702 (2001).
120. J. H. Kim and C. S. Yoon, *Appl. Phys. Lett.* **81**, 3332-34 (2002).
121. K. Nakamura, T. Tokiwa and Y. Kawamura, *J. Appl. Phys.* **91**, 9272-76 (2002).
122. K. Nakamura, *Proc. 13th IEEE Int. Symp. on Appl. Ferroele.*, 389-93 (2002).
123. "Piezoelectric Single Crystals", Ed. by Y. Yamashita, S. Trolier-McKinstry and L. E. Cross, to be published in March (2004).
124. <http://www.atgc.co.jp/div/material/>

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