History and Future Prospect of Electro-ceramics in Japan and Asia

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Abstract

On the background of a long history of Japanese ceramics, various electro-ceramic materials have been studied and many kinds of electronic components using them have been developed in Japan. The first invention of electro-ceramics in Japan should be a ferrite at Tokyo Institute of Technology in 1930, and the mass production of ferrite started in 1937. Then, Japanese electro-ceramic industry has led the world on electro-ceramic materials and components until now, especially in the fields of $BaTiO_3$*, PZT, PTC thermistor, ZnO varistor and insulating ceramics. In recent years, new electro-ceramic materials, their processes and new devices using them have been still studied actively in Japan. Currently, R&D activities in Asia outside of Japan, and electro-ceramic industries in those areas have been grown steadily.*

Key Words: Ferrite, Dielectric ceramics, Piezoelectric ceramics, Semiconductive ceramics, Insulating ceramics, Lead-free material, Base-metal electrode, Nano-particle, Energy harvesting

Introduction

Over the years, various electro-ceramics have been studied and improved in Japan. Using them, Murata and other Japanese manufacturers have been developing and manufacturing many kinds of electronic components. They also lead the worldwide market share of many kinds of electro-ceramic components. As for electro-ceramic components, discoveries or inventions of new materials has promoted to design new electronic components with new functionalities. Hence, the historical progress of material inventions and component industrializations in Japan are overviewed first, and then their current technical trend is overviewed [1].

In Japan, electro-ceramic R&D activities have been still activated, so that some lately topics in this field are also introduced.

Finally, present status of R&D activities and industrialization in Asia outside of Japan is overviewed.

Origin and growth of electro-ceramics in Japan

Japan has a long experience in the field of ceramics. The oldest pottery in Japan was manufactured 16,500 years ago in early Jomon period through radiocarbon dating methods; INTCAL 98 [2]. It is well-known as the oldest pottery in the world which has ever been excavated. The Jomon period is the time in Japanese history from 16,500 to 3,000 years ago. The “Jomon” means “cord-patterned” in Japanese. Pieces of the oldest pottery in Japan are shown in figure 1 [3].

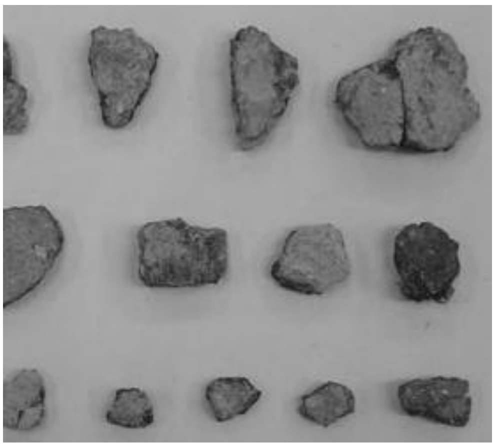


Figure 1. Pieces of the oldest pottery in Japan, 16,500 years ago. This was excavated in Aomori, Japan [3].

On the background of the long history of ceramics in Japan, a lot of Japanese electro-ceramic manufacturers were founded in conventional producing areas of porcelain. For example, Kyocera and Murata were founded in Kyoto, and NGK was founded in Nagoya. These areas are ones of historical producing sites of porcelain table wares in Japan. Until now, many kinds of electro-ceramic components have been developed and produced by Japanese manufacturers using various electro-magnetic properties of ceramic materials. Various electromagnetic properties of ceramics and electronic components using them are summarized in table 1.

Table 1. Electromagnetic properties of ceramics and electro-ceramic components using them.

Electromagnetic property of ceramics	Typical electro-ceramic component
Dielectricity	Multilayer ceramic capacitor, MLCC Planar capacitor, Dielectric duplexer, Dielectric antenna
Piezoelectricity	Filter, Resonator, Gyroscope, Shock sensor, Buzzer, Speaker, Actuator, Sonar
Pyroelectricity	Infrared sensor
Semiconductivity	PTC themistor, NTC thermistor, Varistor
Magnetism	Transformer core, Inductor, Antenna, EMI suppression filter, Isolator
Insulation	High temperature co-fired ceramics, HTCC Low temperature co-fired ceramics, LTCC

Table 2 shows typical electronic equipments and numbers of electro-ceramic components used in them. As shown in table 2, MLCCs of more than 200 are used in only one cellar phone. Because the functionality of electronic equipments is increasing year by year, the number of electro-ceramic components mounted in each equipment is also increasing generally every year. In a case of smart phones, MLCCs of approximately 500 are mounted. The production of advanced ceramics in Japan is increasing year by year so that total sales of electro-ceramics in Japan has been approximately 1,000 B JPY a year since 2006 [4].

Table 2. Typical electronic equipments and numbers of electro-ceramic components used in them.

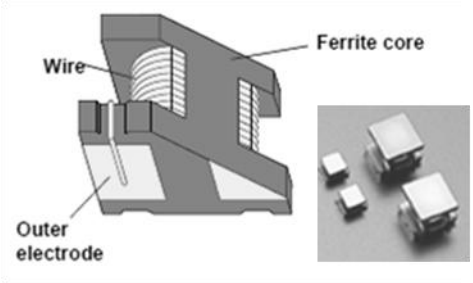
Electro-ceramic component	Electronic equipment	Typical number of use
Chip Multilayer Ceramic Capacitors, MLCC (Dielectrics)	Laptop PC	730
	Cellular Phone	230
	Smart Phone	500
	Digital Camcorder	400
	Car Navigation System	1,000
	Digital TV	1,000
Ceramic Resonators (Piezoelectrics)	Note PC	1
	Digital Camcorder	2
SAW Filters (Piezoelectrics)	Cellular Phone	5
EMI* Suppression Filters (Ferrite)	Note PC	60
	Cellular Phone	20
	Car Navigation System	35
	Digital TV	50
	Digital Camcorder	40

*; Electromagnetic inference

Historical progress of electro-ceramics in Japan and their current technical trends

Ferrite

The first invention of electro-ceramics in Japan should be a ferrite by Kato and Takei of Tokyo Institute of Technology in 1930, and TDK already started the mass production of ferrite core in 1937 [5]. Recently, ferrite ceramics are used in many applications as shown in fig. 1. Especially, EMI suppression filters are increasing rapidly following the progress of digital equipments. Increasing a switching frequency of digital equipments, electromagnetic interference (EMI) noise is increasing. As a result, demand for EMI suppression components increases. Technical trends of ferrite component including EMI suppression filters are downsizing, low profile that means decreasing its height, and corresponding high switching frequency or high current usage. From the viewpoints of ferrite materials and component's structures using them, the optimization for these requirements is applied. Appearances and structures of ferrite inductors are shown in figure 2.



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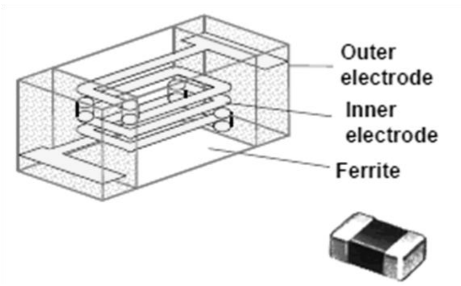


(b)

Figure 2. Appearances and structures of ferrite inductors; wire wound (a) and multilayer (b) types.

Dielectric ceramics

$BaTiO_3$ and its related materials are interesting super-materials in electro-ceramics. The production of $BaTiO_3$ ceramics is much larger than other electro-ceramics [4]. $BaTiO_3$ material was discovered in the US, Russia and Japan during the World War II, almost same time [6, 7]. At that time, it is supposed that there were not any exchanges of information among these nations because of the period of the War. So, these discoveries were seemed to be fulfilled separately. After the discovery of $BaTiO_3$, planer and tubular type ceramic capacitors were manufactured using it, then its applications and productions were broadened by the multilayer ceramic capacitors (MLCCs) using $BaTiO_3$. Especially, MLCCs with base metal inner electrodes without precious metals like Pt, Pd or Ag, pushed its market rapidly because of decreasing their prices. In the early stage of the development of base metal MLCCs, various metals like Cu, Pb or Al were tried to use as inner electrodes, but finally, it was converged to Ni. Ni has good compatibility of enough conductivity as an electronic component and high melting point suitable for sintering $BaTiO_3$ ceramics. In 1970's, a lot of manufacturers in the world competed to develop Ni-MLCCs. In the case of latest MLCC, the chip size is 1.0x0.5x0.5 mm and the capacitance is 10 μF. Dielectric ceramic layers of 0.5 μm thick and Ni electrodes of 0.4 μm thick are laminated alternately. Figure 3 shows progress of decreasing dielectric thickness of MLCCs. These MLCCs of small sizes are used mainly in mobile equipments with the rating voltage 4 or 6.3 V. On the contrary, a demand to high power guaranteed MLCCs is increasing recently for applications in power electrics. These have the rating voltage of up to 1,200 V_{DC}, and they are used, for example, in inverter circuits for electric vehicles. In this case, ferroelectric materials are not suitable because of its large dependence of applied electric field on capacitance, so that paraelectric $BaTiO_3$ ceramics is used mainly.

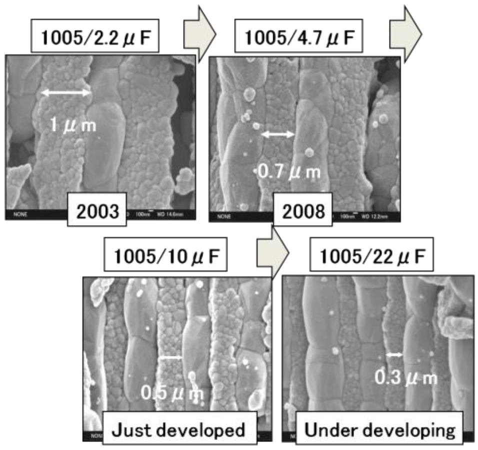
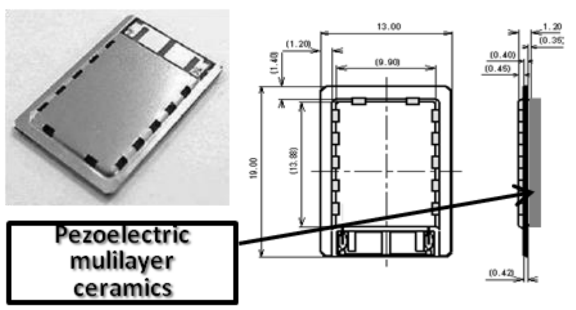


Figure 3. Miniaturization of MLCCs and their change of dielectric thickness; 1005 means MLCC's size of 1.0x0.5x0.5 mm.

Piezoelectric ceramics

Lead Zirconate Titanate (PZT) is well-known as typical piezoelectric ceramics. The high Curie temperature, *Tc*, of $PbZrO_3$ had been already found by Waku in Japan in 1949 [8], after that, the piezoelectricity of PZT ceramics was discovered by Jaffe of NBS in 1954 [9]. Electric filters using PZT ceramics was produced by Murata first in the world in 1963. Then, PZT ceramics has extended its applications from filters, to resonators, buzzers and sensors including sonar, gyroscope and so on. There, piezoelectric resonance has been utilized. Recently, development and industrialization of piezoelectric PZT ceramics as actuators are active. Piezoelectric actuators, utilizing the deformation properties of the piezoelectric ceramics itself, are used for an ink-jet printer head, a fuel-injection system of automobiles, a position control of an autofocus system, an image stabilization system of digital cameras and other many applications. On the contrary, there are new applications utilizing mechanical resonance phenomena like a piezoelectric speaker. The thickness of dynamic speakers, which are in widespread use today, ranges from 2 to 4 mm, while that of piezoelectric speakers can be as thin as 0.5 to 1.2 mm. Moreover, as piezoelectric speakers are of capacitive load, they can dramatically reduce power consumption specifically in the voice band. These features are suitable for mobile equipments. As another example, there is a microblower which is designed to function as an air pump, using the ultrasonic vibrations of piezoelectric ceramics. It can generate high pressure air from a thin and extremely compact unit. In addition to its smaller size, it also offers lower power consumption than more common air-cooling devices, due to the ceramic based drive system. Appearances and structures of a piezoelectric speaker and a microblower are shown in figure 4.



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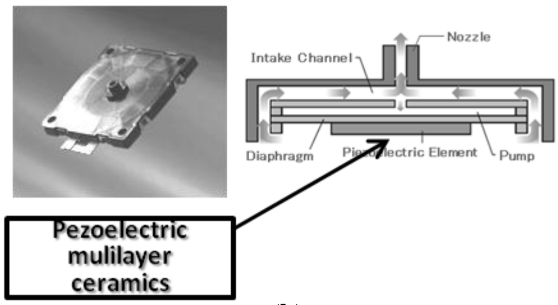


(b)

Figure 4. Appearances of piezoerectric speaker (a) and microblower (b).

Semiconductive ceramics

The semiconductive property of $BaTiO_3$ was patented in 1954 [10]. Saburi of Murata investigated the detailed semiconductive properties of $BaTiO_3$ [11]. Then, first industrialization of PTC thermistor in the world was fulfilled by Murata in 1959 as a heater with automatic temperature controlling. PTC means positive temperature coefficient. Recent progress of PTC thermistor was realization of multilayer structure [12]. $BaTiO_3$ is an insulator; however, it can easily be transformed into a semiconductor by doping a very small amount of a rare earth element such as La. Such semiconducting $BaTiO_3$, which exhibits a small resistivity at room temperature and a large increase in resistivity above *Tc*, is known widely as PTC phenomenon. It is required to decrease the room-temperature resistivity of PTC thermistors to suppress its power consumption. If a PTC element with a multilayer structure can be fabricated, it will have a very low resistance. However, there were some technical issues. The multilayer structure brings the poor withstand voltage. That is because the electric field applied to each grain boundary of the thin layers is larger than that of the bulk type thermistor. Therefore, to decrease the applied voltage per grain boundary, we have to minimize the grain size. Another technical issue is compatibility of sintering conditions. The PTC characteristics are degraded when $BaTiO_3$ is fired in a reducing atmosphere because of desorption of oxygen. On the contrary, the inner electrodes should form an ohmic contact with the *n*-type semiconducting $BaTiO_3$; these electrodes should be composed of a base metal such as Ni and be fired in a reducing atmosphere to prevent the oxidization of the base metal. Therefore, it is difficult to co-fire $BaTiO_3$ with PTC characteristics and an internal electrode. By manipulating composition of $BaTiO_3$ ceramics and its firing process, these issues were solved. Figure 5 shows a decrease of resistance at room temperature by a multilayer structure. As the same semi-conductive ceramics, there is a ZnO varistors. In 1968, Matuoka of Panasonic found a varistor characteristics of ZnO ceramics accidentally during his experiments [13]. Now, these are used widely as circuit protection components.

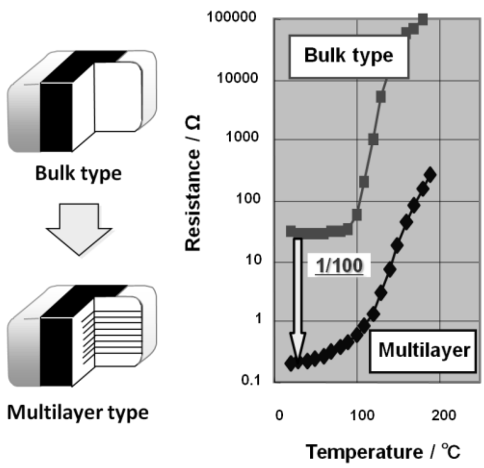
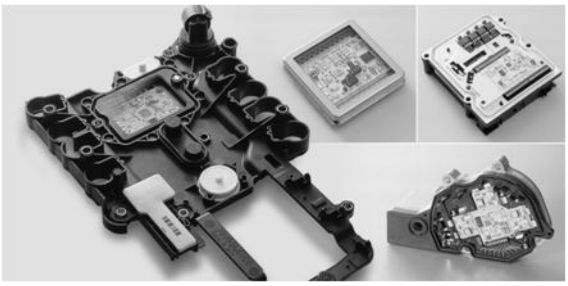


Figure 5. Decrease of resistance at room temperature by multilayer structure of PTC thermistor.

Insulating ceramics

The manufacturing of ceramic insulators was started from 1920's in Germany. Since 1960's, Japanese manufacturers like Kyocera have been developed ceramic substrates and packages following the progress of silicon devices. A multilayer ceramic package was already developed by Kyosera in 1969 [14], then, after 1970's, R&D activities of multilayer substrates like LTCC (Low Temperature Co-fired Ceramics) or HTCC (High

Temperature Co-fired Ceramics) were activated for mainframe computers [15]. Therefore, the R&D activities were held in not only ceramic manufacturers but also computer manufacturers like IBM, Fujitsu, Hitachi, Mitsubishi and NEC. However, the market size of substrates for mainframe computers is not so large, and then this technology of LTCC or HTCC was spread to automobile applications because of its superior reliability at elevated temperatures [16]. Figure 3 shows typical modules using LTCC substrates like ECU or ABS for automobiles. Also LTCC ceramics has been used for modules of wireless communications like Wi-Fi and Bluetooth because of its superior characteristics in high frequency region. Carrier frequencies for wireless communications are increasing gradually from 0.8 to 70 GHz. So, LTCC materials with high-Q values are required, and then ceramics is suitable for this purpose. In figure 6, a band pass filter (BPF) at 26 GHz using LTCC ceramics is also shown, and this is the first surface mounted type component in the frequency range of several 10 GHz [17]. Starting materials of this LTCC is the mixture of glass powder manipulated their composition and spinel-type crystalline powder. During sintering process, almost glass phase is reacted with spinel phase making high-Q crystals. As a result, we can get a LTCC with high-Q value.



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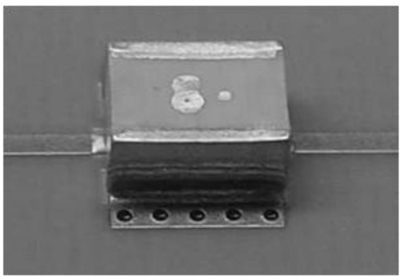


(b)

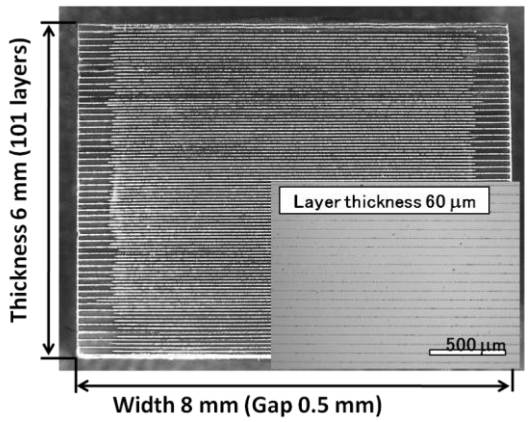
Figure 6. LTCCs for automobile (a) and wireless communication (b) applications.

Future prospect of electro-ceramics in Japan

There are a lot of current activities related to R&D of electro-ceramics in Japan. They cover not only improving properties, but also appropriate technologies and basic technologies. From recent studies, some topics are overviewed.

Actuator of KNN piezoelectric multilayer ceramics with Ni inner electrodes

Recently, piezoelectric actuators have become increasingly important for small mechatronic devices. Ag/Pd alloy is usually used as an inner electrode for multilayer PZT piezoelectric ceramics, however Ag based inner electrode has some disadvantages such as poor electro-migration resistance and expensive cost [18, 19]. In order to overcome these disadvantages, base metal electrodes such as Ni are thought to be useful. At the same time, an increasing awareness of environmental issues has recently prompted active research into lead-free materials, and several candidates were proposed in the basic research stage. In these lead-free materials, $(K,Na)NbO_3$ (KNN) has relatively high piezoelectric constant. Therefore, we investigated the KNN multilayer ceramics with nickel inner electrodes [20]. In figure 7, cross-section of Ni-KNN multilayer ceramics with Ni inner electrodes, of which each piezoelectric layer have 60 μm thickness, and its strain-electric field curves are shown.



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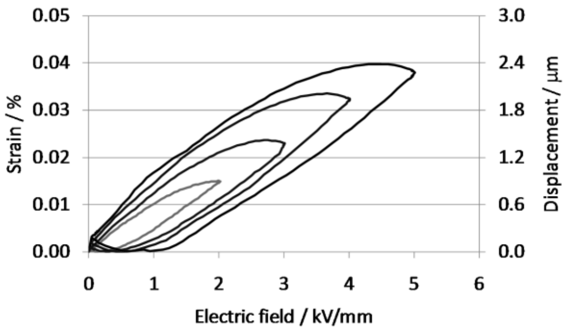


(b)

Figure 7. Cross-section of Ni-KNN multilayer ceramics (a) and its strain-electric field curves (b); each layer thickness of 60 μm.

Thin film capacitor and nano-particles of ferro-electric material

Using conventional ceramic green process, it is difficult to fabricate multilayer structure where a thickness of each layer is less than 100 μm. One solution is a film formation by a chemical solution deposition method with a spin coating technology. Typical capacitor using CSD method is shown in figure 8 [21].

In fig. 8, the thickness of dielectric layer is 90 nm and the size of dielectric grain is less than 20 nm. When we fabricate these kinds of thin film capacitors, the minimum grain size of ferroelectric materials which hold ferroelectricity is interested issue. Examining this problem, thin films were made by spin coating and subsequent heat treatment of nano-particles of $BaTiO_3$ fabricated by a micro-emulsion method [22]. The dependence of grain size on D-E hysteresis is shown in figure 9. From fig. 9, we can understand that the minimum grain size, which holds ferroelectricity, is more than 18 nm.

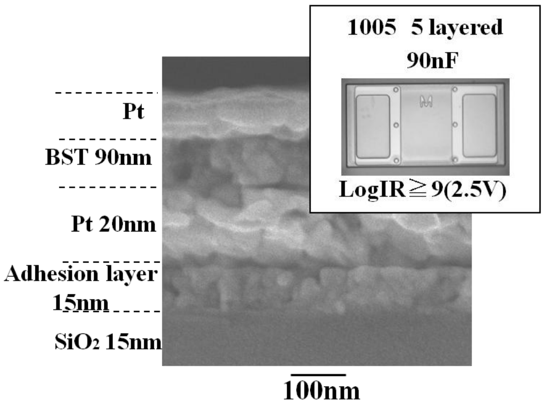


Figure 8. Miniaturization of MLCCs and their change of dielectlic thickness; 1005 means MLCC's size of 1.0x0.5x0.5 mm.

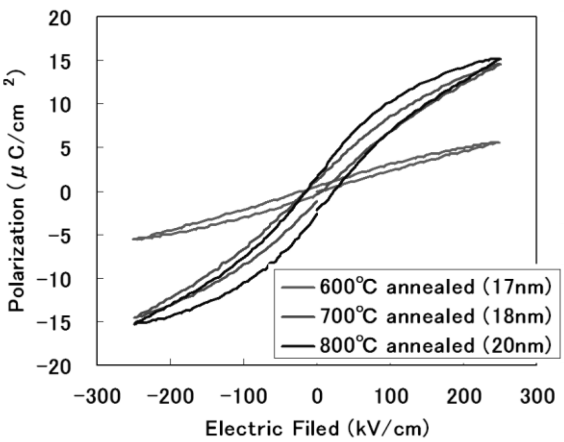
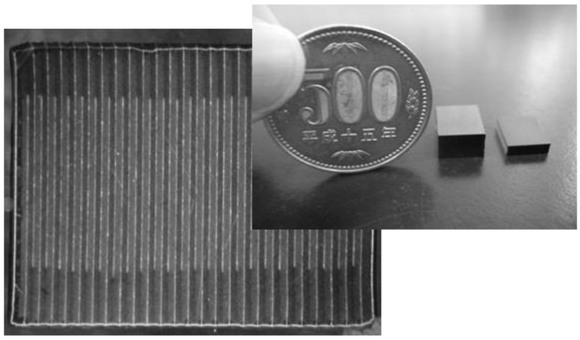


Figure 9. Dependence of grain size on D-E hysteresis of spin coated thin films using nano-size $BaTiO_3$.

Multilayer ceramics used for energy harvesting

Reacently, applications of electro-ceramic materials and processes to energy harvesting have been studied actively. In many cases, multilayer strictures are utilized. For materials, ceramic electrolytes, ceramic conductors, piezoelectric ceramics and other ceramics are used. In order to realize multilayer structures, co-firing process is usually used. In figure 10, examples of piezoelectric vibration generator [23], thermoelectric generator [24] and planar SOFC [25] are shown. These devices for energy harvesting have characteristics of compact and light, because multilayer structures can increase their figure of merit par their volume.

(a)



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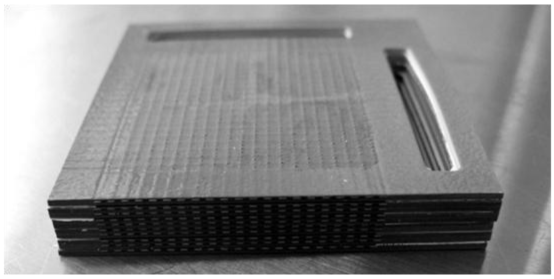

(c)

Figure 10. New applications of multilayer electro-ceramics; piezoelectric vibration generator (a) , thermoelectric generator (b) and planar SOFC (c).

Present status of electro-ceramics in Asia

Currently, electro-ceramic industries in Asia without Japan have been growing year by year. Moreover, a lot of R&D activities are operated in various organizations including governmental institutes and universities.

In the case of MLCC manufacturers, Asian companies without Japanese ones hold large market share. Figure 11 shows global market share of MLCC sales in 2011/Q1. As shown in this figure, electro-ceramic industries in Asia outside of Japan have been growing year by year.

According to the R&D activities, the Asian Meeting on Electroceramics (AMEC) has been held every two years. Last meeting (AMEC-7) was held in 2010 at Jeju, Korea in conjunction with the 7th Asian Meeting on Ferroelectricity (AMF-7) [26], where the oral presentations more than 200 papers were read and the posters over 500 were presented. The fields presented were included not only conventional electro-ceramics but fundamental and cutting edge technologies. Those presenters were from Japan, Korea, China, Taiwan, India, Malaysia, Thailand, Singapore and other Asian countries. This shows that R&D activities in these areas have been carried out actively. The next meeting (AMEC-8) is going to hold this July at Penang, Malaysia.

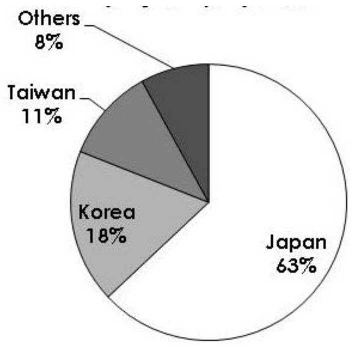

Figure 11. Global market share of MLCC in 2011/Q1; this data was estimated by Murata.

Summary

The origin of Japanese ceramics was explained, then subsequence history of material inventions and component industrializations in Japan were overviewed including ferrite, dielectric, piezoelectric, semiconductive and insulating ceramics. Here, it was obviously that Japanese electro-ceramic R&D activities and their industrializations have been played one of leading roles in the world.

From the recent studies of electro-ceramics in Japan, some topics were presented including an actuator of KNN piezoelectric multilayer ceramics with Ni inner electrodes, a thin film capacitor and nano-particle of ferroelectric material and multilayer ceramics used for energy harvesting.

Present status of electro-ceramics in Asia outside of Japan was briefly introduced. Currently, electro-ceramic industries in Asia without Japan have been growing year by year as the case of MLCC's manufacturers. The R&D activities in those areas have been also activated in the field of not only conventional electro-ceramics but cutting edge technologies. The presence in those areas will further increase in the world near future.

Acknowledgments

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