

# Innovative nanocrystal-based technologies for ceramic devices with novel electronic functions

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**Abstract:** There has been a great progress in the synthesis of a variety of inorganic colloidal nanocrystals (NCs) with highly controlled size and shape in the last decade. This achievement has promoted comprehensive researches on the fabrication and engineering of NC devices with novel structure and function with the aim of utilizing them in a wide area of applications, including electronics and optoelectronics, by using various NC assembling and patterning methods. However, colloidal NCs having been extensively investigated so far are mostly metals, semiconductors and magnetic materials, and only limited investigations on oxide NCs from a point of view of NC ceramic engineering have been done. Here, innovative nanocrystal-based technologies necessary for the fabrication of NC ceramic devices with novel and gigantic electronic functions, limiting the materials to perovskite oxides, and a new perspective on the future ceramic technology are discussed.

**Key words:** nanocrystals; electronic functions; Perovskite; bottom-up process

## 1 Introduction

There has been a great development in the ceramic technology based on powder processing in the last three decades, and ceramic devices with a variety of electronic functions have been manufactured thereby. The powder-processing-based ceramic technology owes its striking development to marked progresses in both technologies of producing starting ceramic powder and of forming device structures. The early ceramic powder synthesis technology, based on solid-state reaction methods, has made a rapid advance by adopting the advantage of solution-phase synthesis

methods, which allow production of ceramic powder with high purity and much homogeneous grain morphologies (size and shape). It is now possible to obtain various kinds of electronic ceramic powder with well-controlled particle sizes in the range from nanometer to micrometer by employing suitable solution methods, and one may easily find many reports on the synthesis of nanocrystalline particles of perovskite oxides, which are used in the largest quantity in the electroceramic industry [1-4]. As to the technology of fabricating device structures, since most electronic ceramic devices have been used in rather simple forms of disks and slabs unless their forms cannot give desired electronic functions, the development of techniques for making two- and three-dimensional functional structures with purpose of generating new electronic functions has little

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progressed. However, from a keen demand for continuing downsizing of ceramic devices, such as capacitors and inductors, used in large quantity as key elements in microelectronic circuits, the technology of forming and stacking thin ceramic (green) sheets into a multilayer structure with a uniform thickness of sintered ceramic layers (namely, interelectrode spacing) has greatly advanced to allow successful production of multilayer ceramic chip devices with highly enhanced electronic functions. The state-of-the-art technology enables to fabricate a multilayer structure with an interelectrode spacing of around  $1\ \mu\text{m}$  [5], and the commercialization of multilayer ceramic chip capacitors, with the smallest size of 2012 ( $2.0\ \text{mm} \times 1.25\ \text{mm}$ ), with extremely large capacitance values of  $>22\ \mu\text{F}$  has recently been realized by Murata Co. Similar fabrication techniques for multilayer tip-type devices have been applied to other electronic ceramics, including thermistors [6], varistors [7], and inductors [8], resulting in a considerable success in the improvement of the performance of their devices. However, since the current powder processing-based ceramic technology has substantial technical limitations that hardly allow creating two- and three-dimensional ceramic nanostructures with feature sizes of  $<100\ \text{nm}$ , it is essential to develop innovative nanocrystal-based ceramic technology comparable with the photolithography-based semiconductor (or silicon) technology to open a new horizon in the field of electronic ceramics.

Photolithography as the central technique in the semiconductor technology has been most successful in manufacturing microelectronic structures, by which it is technologically possible to fabricate almost all three-dimensional even complex microstructures designed to let new phenomena occur. However, little benefit can be derived from the semiconductor technology when used to fabricate ceramic nanostructures because of great disadvantages with its time-consuming and costly processing and poor applicability to ceramic materials of particularly multicomponent systems. For further developments in the electronic ceramic industry, an alternative technology of manufacturing ceramic nanostructures needs to be developed, but such technology has not systematically and intensively been investigated yet.

To resolve this issue it would be most effective to establish a robust technology of assembling NCs into electronic ceramic devices with novel functional structures. In this regard, there have been extensive

researches on the methods for organizing (assembling) NCs into specific ordered arrays and patterned structures toward various electronic applications. By various NC assembling processes with and without combination of lithography-assisted patterning methods novel three-dimensional NC structures, including NC superlattices as a typical example, and some electronic and optoelectronic NC devices have been successfully fabricated. Detailed and comprehensive information of these NC superlattices and devices can be found in some articles [9-12].

Here, we study a subject on the fabrication of NC ceramic devices with gigantic electronic functions (GEFs), including relaxor and PCTR (positive temperature coefficient of resistivity), derived from novel nanostructures constructed, taking such a nanostructure, as a model system, as is schematically shown in Fig. 1, and discuss sophisticated techniques required to fabricate such NC devices, limiting the materials of NCs to perovskite oxides, and technical problems to be solved.

## 2 Synthesis of Perovskite NCs with a cubic shape (nanocubes)

There have been numerous researches on the synthesis of colloidal monodisperse NCs with well-controlled morphology and structure of a wide variety of materials, including metals [13,14], semiconductors [14,15], and oxides [14,16], using various solution-phase methods such as hydrothermal/solvothermal [17],

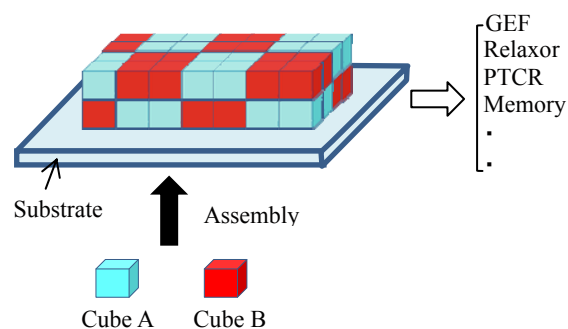


Fig. 1 A schematic image of a NC device (nanostructure) fabricated using NC cubes and examples of gigantic electronic functions (GEFs) derived from novel nanostructures. Assembly of nanocubes is assumed to be carried out using those monodispersed in proper solutions. PCTR denotes Positive Temperature Coefficient of Resistivity.

hot-injection/decomposition [18], sol-gel (aqueous/nonaqueous) [19], and liquid-solid-solution [20] routes. To fabricate NC devices with novel structure and function it is first of all necessary to produce NCs with precisely controlled morphology and structure, and the size and shape control of NCs has been achieved to a large extent for metal, magnetic and semiconductor materials. Murray group has succeeded in the synthesis of a variety of colloidal nanoparticles with precise values of size and shapes designed, and they have accomplished most impressive achievements in the fabrication of three-dimensional binary nanoparticle (nanocrystal) superlattices (BNSLs) with diverse structures, using spherical nanoparticles with different sizes [9]. In Fig. 2 are shown some examples of BNSLs fabricated by his group using a self-assembly process based on the solvent-evaporation-deposition (SED) method mentioned below, in which their TEM images of the characteristic projections and modeled unit cells of the corresponding 3-D structures are presented.

In previous researches on the fabrication of functional nanostructures spherical nanoparticles have mainly been used; however, to create highly dense NC structures cubic NCs (NC cubes) are favorable for using as building blocks since assembly of NC cubes theoretically allow creation of a NC structure of nearly full dense, as seen from the schematic shown in Fig. 1.

As to the synthesis of perovskite oxide nanoparticles, including  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  NCs, there have appeared a large number of reports in the literature; however, limiting the items to monodisperse  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  nanocubes, related reports are quite small in number. Examples of monodisperse  $\text{BaTiO}_3$  and  $\text{SrTiO}_3$  NCs with well-developed cube-like shapes are shown in Fig. 3; the  $\text{BaTiO}_3$  nanocubes were synthesized by a soft solution chemical process using  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ti}(\text{O}i\text{Bu})_4$ ,  $\text{BuOH}$  and oleic acid at  $135^\circ\text{C}$  under a strong  $\text{NaOH}$  basic condition [21], while the  $\text{SrTiO}_3$  nanocubes were prepared from an aqueous solution containing  $\text{Sr}(\text{OH})_2$ , bis(ammonium lactate) titanium dihydroxide (TALH), hydrazine and oleic acid using a hydrothermal process at  $200^\circ\text{C}$  under a strong  $\text{NaOH}$  basic condition [22]; the latter was modified from that proposed by Koumoto group [23]. It can be presumed that organic molecules used in the solvothermal/hydrothermal processes, which act as ligand and/or surfactant molecules, play important roles in the formation of cubic NCs in these cases, but the forming mechanisms of these NC cubes have not been satisfactorily clarified yet. A strict understanding of the NC size/shape-control mechanism in these rather simple systems, by carrying out much closer investigations under strictly controlled synthesis conditions, will lead to a significant success in the synthesis of high quality monodisperse perovskite

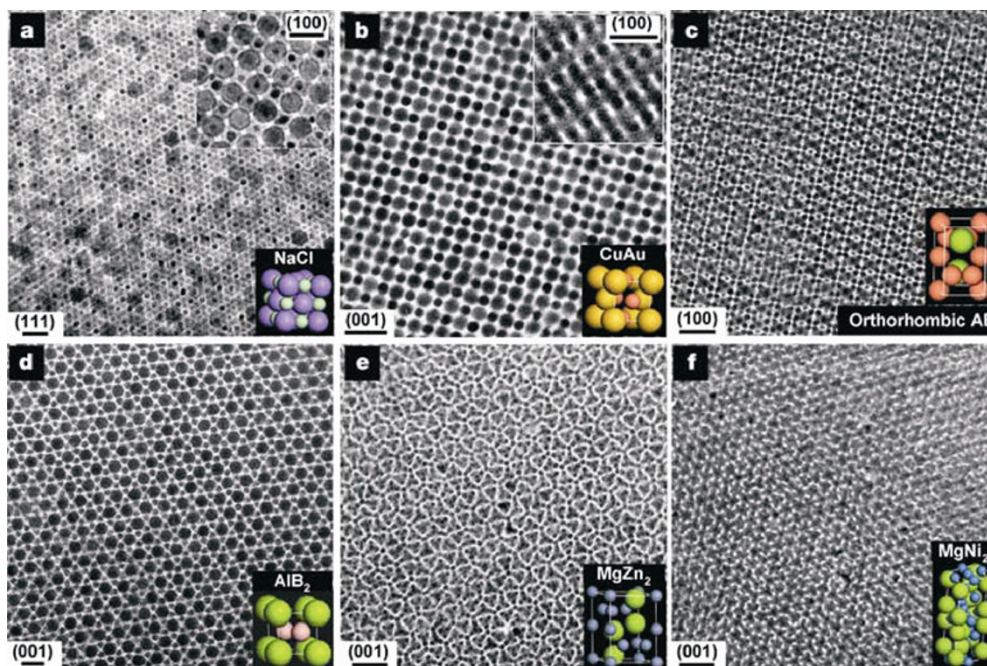


Fig. 2 TEM images of the characteristic projections of binary superlattices (BNSLs), self-assembled from different NCs, and modeled unit cells of the corresponding 3-D structures. Reprinted from Ref. [9].



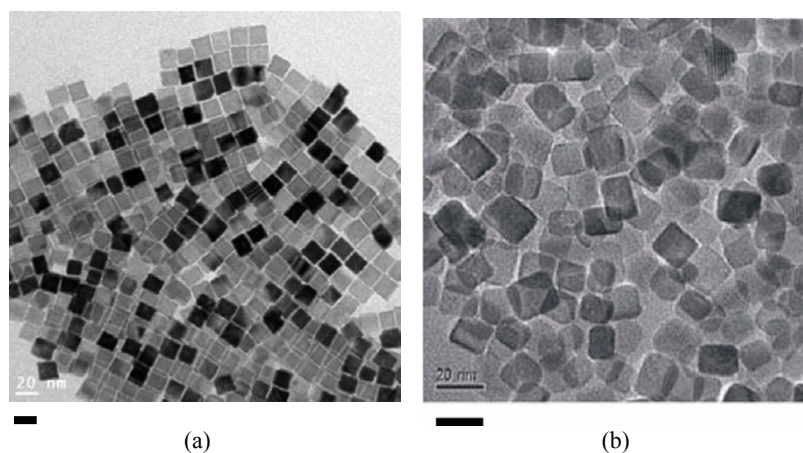


Fig. 3 TEM images of (a) BaTiO<sub>3</sub> nanocubes, reprinted from Ref. [21] and (b) SrTiO<sub>3</sub> nanocubes., reprinted from Ref. [22]. Bars = 20 nm.

nanocubes with a size desired and its narrow size distribution.

### 3 Assembly of NC cubes into functional nanostructures

There have been a variety of methods for fabrication of NC devices with electronic functional structures using various NC assembly techniques such as SED [24], liquid-air-interface (LAI or LB: Langmuir-Blodgett) [25], spin-coating/dip-coating layer-by-layer (LBL) [26], and surfactant-mediated-aggregation (SMA) [27] processes, together with lithography-assisted patterning processes. Of these, outlines of SED, LAI and SMA processes are schematically shown in Fig. 4. Since the methods of spin-coating and dip-coating processes are simple and unnecessary to be described, schematics of these processes are not shown in the

figure. As mentioned above, it has been proved that the SED-based assembly process enables to construct excellent BNSL structures. This method is simple and easy to use for assembling particularly spherical NCs into dense (nearly close-packed) nanostructures, but that it requires a strict control of the evaporation condition of solvent to fabricate free-of-disorders BNSLs should also be mentioned. Dong et al. [25] has successfully fabricated BNSL magnetoresistive devices using a LAI technique; in Fig. 5 are shown schematics of the processes of BNSL membrane growth and transferring it on a substrate prepatterned with metal electrodes in (a) and the device fabricated in (b). The LAI method can be used for NCs with various shapes such as spheres, cubes, and rods, and has its advantages of allowing the construction of large-area single- and multi-component NC membranes on various kinds of substrate including thin polymer sheets; the membrane growth and transfer processes

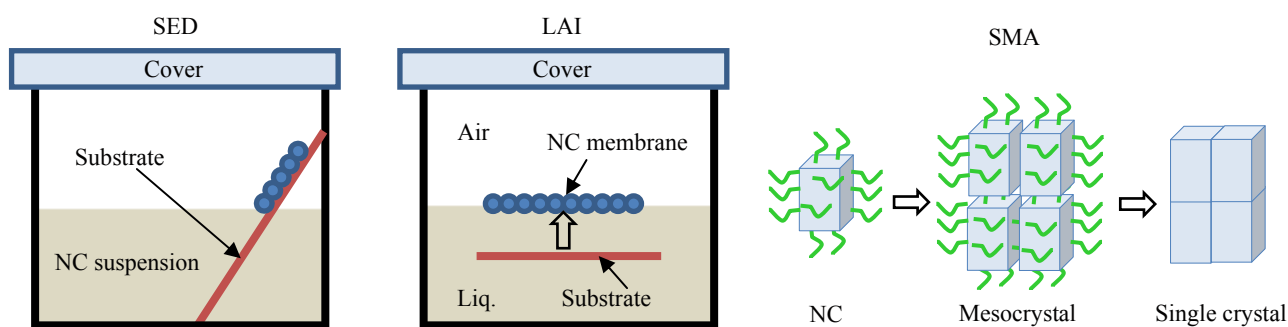


Fig. 4. Schematics of solvent-evaporation-deposition (SED), liquid-air-interface (LAI) and surfactant-mediated-aggregation (SMA) processes. The SMA process describes a growth mechanism of single crystals, in which a mesocrystal intermediate is formed by surfactant-mediated-assembly of NCs, then transforming into a single crystal by crystallographic fusion of the oriented building units through the oriented attachment mechanism.

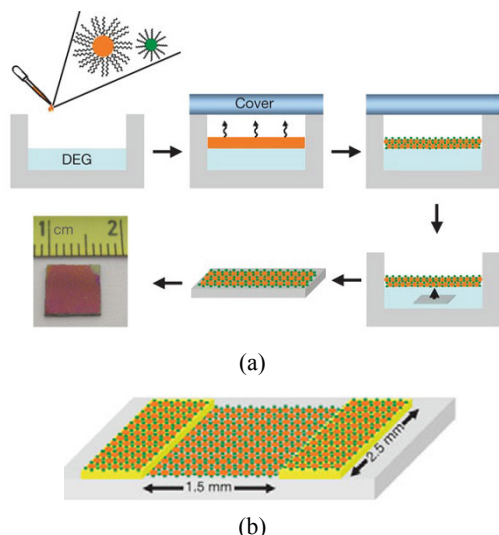


Fig. 5 (a) Schematics of a BNSL membrane growth and transfer process onto a substrate and (b) a NC device fabricated. Reprinted from Ref. [25].

need to be properly modified according to the system of NCs used, though. The LAI method may significantly enhance its advantage by involving role-to-role processing. The LBL method combined with spin-coating and dip-coating processes has also been widely used for fabricating NC devices, and many examples of successful fabrication of electronic/optoelectronic NC devices, such as field-effect transistors, photodetectors, and solar cells, have appeared in the literature [28,29]. However, since spin-coating and dip-coating methods are considered to hardly allow assembling of NC cubes into nearly full dense membranes, these methods are not suitable for the fabrication of ceramic devices using nanocubes. As to the SMA process, it describes a growth mechanism of single crystals via a mesocrystal intermediate

formed by surfactant-mediated-assembly of NCs, which then transform into a single crystal by crystallographic fusion of the oriented building units through the oriented attachment (OA) mechanism, as shown in Fig. 4c. It may be worthy to note that mesocrystals have characteristic faceted external structures, and a nearly perfect crystallographic alignment of the constituent NCs can be seen in them. The growth mode of single crystals by the OA mechanism, which is different from a classical one known as the Ostwald ripening mechanism, was first reported by Banfield et al. [30] for the case of anatase ( $\text{TiO}_2$ ) aggregates composed of coarsened primary nanoparticles obtained under hydrothermal aging conditions. Since then, many reports on the OA phenomenon observed for NC aggregates of a variety of materials, including CeO and ZnO, synthesized via solution-phase routes have appeared in the literature [31,32]. The SMA process associated with the phenomenon of OA-based crystallographic fusion between NC particles is expected to allow a successful fabrication of NC structures with high electronic transport characteristics, leading to the development of intriguing and sophisticated techniques for fabricating NC ceramic devices with superior electronic functions. One may find comprehensive and much detailed descriptions of SMA and OA in some articles and reviews [33,34].

Figure 6 shows a schematic of a route that the author propose to the fabrication of NC ceramic devices on polymer sheets via an LAI or SMA method, in which charged NC cubes to be assembled and transferred on a substrate by electrostatic forces are used as building blocks. There have been many investigations on the creation of NC structures using

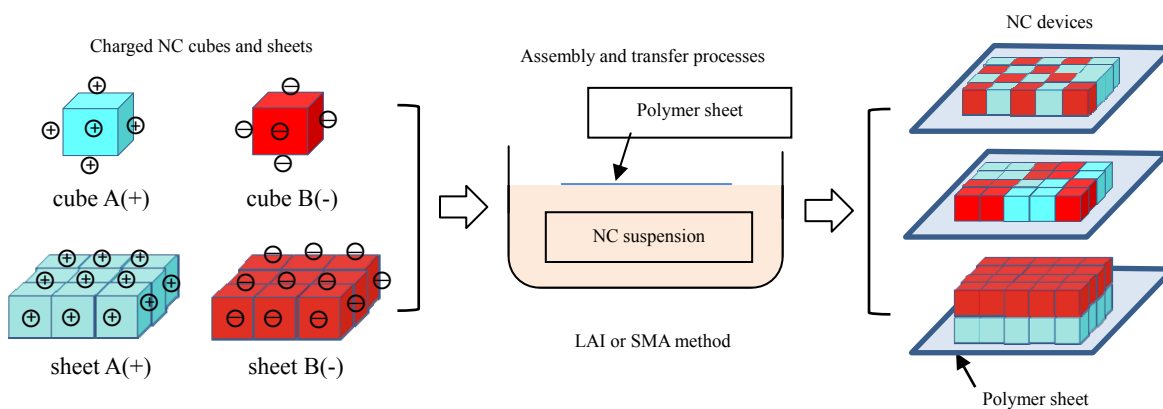


Fig. 6 Schematic of a method for the construction of NC devices on polymer sheets, in which charged NC cubes and electrostatic-force-based assembly and transfer processes by the LAI or SMA method are used.

electrostatic forces, and successful fabrication of many unique nanostructures, including binary superstructures, has been reported [35,36]. However, since the shape of charged nanoparticles used in the previous researches was almost limited to spherical NCs with few exceptions for metal nanocubes, we need to develop innovative processing techniques that allow the electrostatic assembly of nanocubes into close-packed nanostructures. The author cannot disclose at present any concrete ideas for the realization of such techniques, but some experimental results concerning the fabrication of nanoparticulate layers and films on electrically patterned substrates may give a hint for solving the problems concerned [37,38].

#### 4 Nanocrystal ceramic devices with novel electronic functions

Figure 7 shows one example of NC ceramic devices with novel electronic functions, in which a schematic of a NC device made up of two kinds of ferroelectric (or dielectric) perovskite nanocubes assembled to form a specific polar domain structure, so-called polar nanoregion (PNR) inside which local spontaneous polarization exists, along with relaxor-type dielectric properties expected for the NC device. In Fig. 7 is also shown relaxor-like dielectric properties obtained for a

free-standing dense ceramic sheet consisting of BaTiO<sub>3</sub> NCs with a median size of 57 nm [39]. This experimental fact provides a promising clue in considering the NC structures to be constructed for realizing NC devices with novel, gigantic dielectric functions based on relaxor-type dielectric responses. In the figure,  $T_d$  indicates so-called Burns temperature [40], below which PNRs exist; the free-standing BaTiO<sub>3</sub> NC ceramic sheet was confirmed to exhibit a definite (but slim) ferroelectric hysteresis loop at temperatures above the Curie point  $T_c$  up to around 150 °C. Since intensive researches on relaxor ferroelectrics by Cross group [41] following the pioneering work of Smolenskii, there have been made a large number of investigations on the relaxor characteristics of complex perovskite materials, including Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> (PMN) as a representative one, with enormous interest from theoretical and engineering points of view. Since the relaxor dielectric behavior, characterized by a broad peak of dielectric constant with its large frequency dependence, has been observed in a variety of complex perovskite ferroelectrics, various models of the mechanism, including a diffuse phase transition (DPT) and spin-glass models, based on compositionally disordered structures have been proposed. However, recent theoretical and experimental (using X-ray and neutron analyses) studies have revealed that the origin

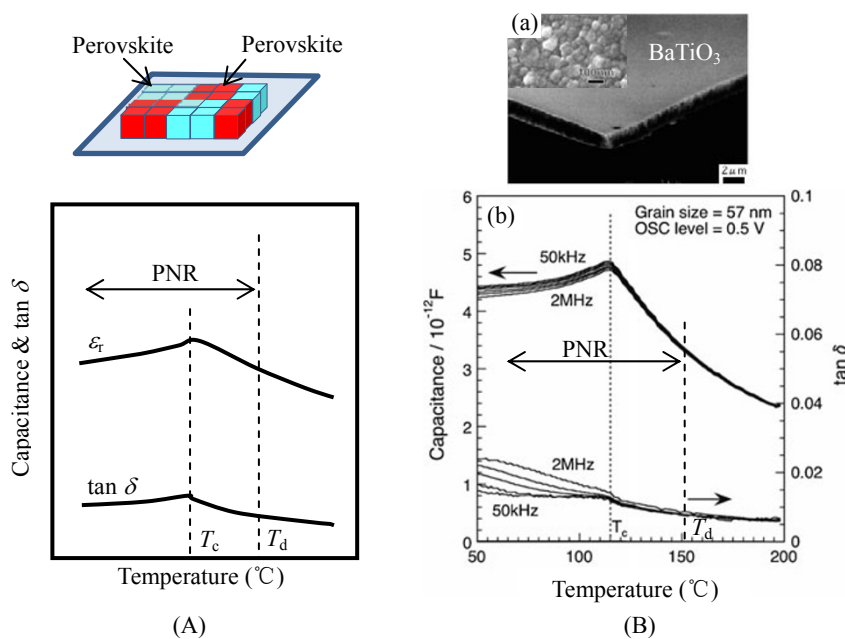


Fig. 7 (A) Schematic of a NC device with a specific polar domain structure and relaxor-type dielectric responses expected for the device, and (B) (a) SEM image of a free-standing BaTiO<sub>3</sub> NC ceramic sheet and (b) its dielectric properties observed.

of relaxor is closely connected with the existence of PNRs induced by factors other than the structural phase transition seen in normal ferroelectrics. Various probable factors, including chemical/lattice disorder, stress/strain, grain size, and electric-field, which can induce the formation of PNRs through local fluctuations of spontaneous polarization, have been proposed, being still a point of controversy. In connection with this, if we are able to create such NC structures, for example, using BaTiO<sub>3</sub> and SrTiO<sub>3</sub> nanocubes, as those involving an effective PNR-inducing factor, lead-free NC ceramic devices with relaxor-type gigantic dielectric functions will be realized.

Figure 8 shows a new type of PTCR ceramic device made of a semiconducting BaTiO<sub>3</sub> NC sheet, taken as an example of NC ceramic devices with gigantic, intriguing semiconducting functions, for the realization of low-resistance flexible PTCR ceramic sheets being expected for applications in various areas including battery, medical science, and aerospace, as resettable circuit protection devices. The PTCR characteristic has been well known to be a grain boundary property of semiconducting BaTiO<sub>3</sub> ceramics, and the Heywang-Jonker model has widely been accepted as one explaining most sufficiently its mechanism. The model explains the low-resistance of the PTCR characteristic below  $T_c$  by the effect of spontaneous

polarization and the anomalous increase of resistance above the temperature by the decrease in dielectric constant of the materials according to the Curie-Weiss law [42]. The present author et al., however, has found the fact that many single grain boundaries in thin ceramic bars consisting of semiconducting BaTiO<sub>3</sub> (doped with La) grains sintered together in series exhibit saw-tooth type PTCR characteristics, characterized by an abrupt increase in resistivity at  $T_c$ , followed by a monotonous decrease in it, as shown in Fig. 8 [43]. The saw-tooth type PTCR characteristic can be hardly explained by the decrease of dielectric constant obeying the C-W law alone, and to well explain the fact the effect of strain- and electric field-induced polarization still existing above  $T_c$  needs to be taken account [44]. Regarding to the proposed PTCR ceramic nanostructure shown in Fig. 8, establishing a procedure to generate spontaneous polarization at both surface regions of the BaTiO<sub>3</sub> nanocube sheet sandwiched with thin flexible conducting polymer sheets acting as electrodes is essential in the technology of fabricating this device. Any clear solutions for this problem have not been found yet, but the experimental results reporting the induced ferroelectricity in stained BaTiO<sub>3</sub> and SrTiO<sub>3</sub> thin films may provide some hints to solve the problems [45-47].

The technology of fabricating such NC ceramic

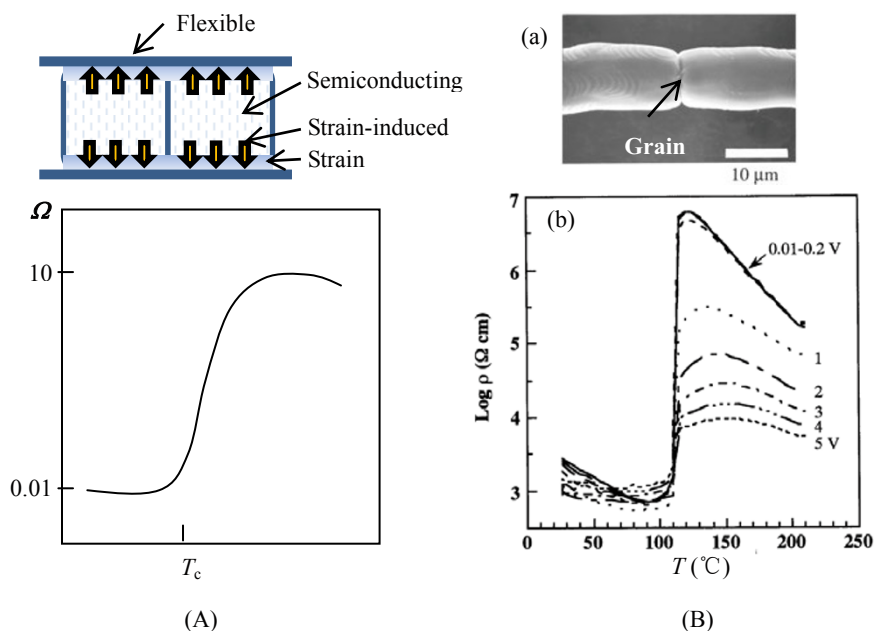


Fig. 8 (A) Schematic of a new type of PTCR device made of a semiconducting BaTiO<sub>3</sub> NC sheet and a low-resistance PTCR characteristic caused by strain-induced polarization generated in the NC sheet, and (B) (a) SEM image of a thin single-grain-boundary BaTiO<sub>3</sub> ceramic bar and (b) single-grain-boundary PTCR characteristics observed.



devices as are shown in Figs. 7 and 8 involves many problems which need to be solved; some of the essential problems are (a) synthesis of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> NCs with a regular cubic shape and narrow size distribution (<10% standard deviation: SD), (b) crystallographic contact between nanocubes for providing them with good electronic interconnection, and (c) formation of novel electronic functional structures in NC ceramic devices. In regard to the problem (a), a number of investigations have been made of shape-control synthesis of metal NCs via solution-phase routes, and close understanding of the nucleation and growth mechanisms of a variety of metal NCs has been made possible. As a result, the technology of forming metal NCs with specific shapes has been established, which has allowed the synthesis of monodisperse nearly perfect cubic NCs of fcc (face-centered-cubic) metals, such as Ag, Au, and Pd [48]. However, the methodology established for the fcc metal systems is, basically, hardly extended to the systems of BaTiO<sub>3</sub> and SrTiO<sub>3</sub>, so we need to establish procedures suitable for the systems. To this end, a deep insight into the forming mechanisms of BaTiO<sub>3</sub> and SrTiO<sub>3</sub> nanocubes synthesized in the previous studies [21,22] should be effective. For the problem (b), making use of the OA phenomenon mentioned above seems to be effective to gain a most promising solution. To that end we need to establish a procedure for either replacing original surface ligands, particularly long-chain surfactant molecules such as oleic acid, with small molecules or removing them under proper pH conditions. The problem (c) is very difficult to find its solutions by current NC technology, but the author think that the introduction of local strains at specific sites of a nanostructure can be an effective solution and a challenging task in the NC technology of interest.

## 5 Summary and outlook

In this paper, a future prospect, with author's expectation for the next generation electronic ceramics, of the NC technology of fabricating ceramic devices with novel, gigantic electronic functions, which has attracted great interest in its potential for introducing a radical technical innovation into the current powder-based ceramic technology, is described. Since there have been many excellent reviews on the size/shape-controlled synthesis of colloidal NCs of a variety of materials and NC assembly technologies to

construct electronic functional nanostructures, to avoid a mere reintroduction of such NC technologies and to make the point of the NC technology here concerned clear, the author here took up two NC ceramic devices of relaxor and PTCR, as representative examples relating to gigantic electronic functions, and NC technologies of the synthesis and assembly of perovskite oxide nanocubes, particularly BaTiO<sub>3</sub> and SrTiO<sub>3</sub> nanocubes as building blocks in those cases. Since there have been only a few/few researches on the synthesis of perovskite oxide NCs with a regular cubic shape and a narrow size distribution of <10% SD and on the creation of nanostructures by assembly of oxide nanocubes, almost new, sophisticated NC technology needs to be established. The establishment of an innovative NC-based technology for ceramic devices with novel electronic functions is a challenging task in the field of electroceramics and is expected to be achieved in the near future.

## References

- [1] Pithan C, Hennings D, Waser R. Progress in the Synthesis of Nanocrystalline BaTiO<sub>3</sub> Powders for MLCC. *Int J Appl Ceram Technol* 2005, **2**: 1-14.
- [2] Demirörs AF, Imhof A. BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, CaTiO<sub>3</sub>, and Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> particles: A general approach for monodisperse colloidal perovskites. *Chem Mater* 2009, **21**: 3002-3007.
- [3] Dong W, Li B, Li Y, *et al.* General Approach to Well-Defined Perovskite MTiO<sub>3</sub> (M = Ba, Sr, Ca, and Mg) Nanostructures. *J Phys Chem* 2011, **115**: 3918-3925.
- [4] Yan T, Liu XL, Wang NR, *et al.* Synthesis of monodispersed barium titanate nanocrystals—hydrothermal recrystallization of BaTiO<sub>3</sub> nanospheres. *J Crystal Growth* 2005, **281**: 669-677.
- [5] Polotai AV, Fujii I, Shay DP, *et al.* Effect of heating rates during sintering on the electrical properties of ultra-thin Ni–BaTiO<sub>3</sub> multilayer ceramic capacitors. *J Am Ceram Soc* 2008, **91**: 2540-2544.
- [6] Niimi H, Mihara K, Sakabe Y, *et al.* Preparation of multilayer semiconducting BaTiO<sub>3</sub> ceramics co-fired with Ni inner electrodes. *Jpn J Appl Phys* 2007, **46**: 6715-6718.
- [7] Wan S, Lu W, Wang X. Low-temperature sintering and electrical properties of ZnO-Bi<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-Co<sub>2</sub>O<sub>3</sub>-MnCO<sub>3</sub>-Based varistor with Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> frit for multilayer chip varistor applications. *J Am Ceram Soc* 2010, **93**: 3319-3323.



- [8] Krishnaveni T, Kanth BR, Raju VSR, *et al.* Fabrication of multilayer chip inductors using Ni–Cu–Zn ferrites. *J Alloy Comp* 2006, **414**: 282-286.
- [9] Shevchenko EV, Talapin DV, Kotov NA, *et al.* Structural diversity in binary nanoparticle superlattices. *Nature* 2006, **439**: 55-59.
- [10] Overgaag K, Evers W, Nijs B, *et al.* Binary superlattices of PbSe and CdSe nanocrystals. *J Am Chem Soc* 2008, **130**: 7833-7835.
- [11] Talapin DV, Lee JS, Kovalenko MV, *et al.* Prospects of colloidal nanocrystals for electronic and optoelectronic applications. *Chem Rev* 2010, **110**: 389-458.
- [12] Luther JM, Law M, Beard MC, *et al.* Schottky solar cells based on colloidal nanocrystal films. *Nano Lett* 2008, **8**: 3488-3492.
- [13] Xia Y, Xiong Y, Lim B, *et al.* Shape-controlled synthesis of metal nanocrystals: Simple chemistry meets complex physics? *Angew Chem Int Ed* 2009, **48**: 60-103.
- [14] Park J, Joo J, Kwon SG, *et al.* Synthesis of monodisperse spherical nanocrystals. *Angew Chem Int Ed* 2007, **46**: 4630-4660.
- [15] Rogach AL, Talapin DV, Shevchenko EV, *et al.* Organization of matter on different size scales: Monodisperse nanocrystals and their superstructures. *Adv Funct Mater* 2002, **12**: 653-664.
- [16] Jeong U, Teng X, Wang Y, *et al.* Superparamagnetic colloids: Controlled synthesis and niche applications. *Adv Mater* 2007, **19**: 33-60.
- [17] Clark IJ, Takeuchi T, Ohtoric N, *et al.* Hydrothermal synthesis and characterisation of BaTiO<sub>3</sub> fine powders: Precursors, polymorphism and properties. *J Mater Chem* 1999, **9**: 83-91.
- [18] Murray CB, Sun S, Doyle H, *et al.* Monodisperse 3d transition-metal (Co, Ni, Fe) nanoparticles and their assembly into nanoparticle superlattices. *MRS Bull* 2001, **26**: 985-991.
- [19] Chandler CD, Roger C, Hampden-Smith MJ. Chemical aspects of solution routes to perovskite-phase mixed-metal. *Chem Rev* 1993, **93**: 1205-1241.
- [20] Wang X, Zhuang J, Peng Q, *et al.* A general strategy for nanocrystal synthesis. *Nature* 2005, **437**: 121-124.
- [21] Adireddy S, Lin C, Cao B, *et al.* Solution-based growth of monodisperse cubic-like BaTiO<sub>3</sub> colloidal nanocrystals. *Chem Mater* 2010, **22**: 1946-1948.
- [22] Dang F, Mimura K, Kato K, *et al.* Growth of monodispersed SrTiO<sub>3</sub> nanocubes by thermohydrolysis method. *CrstEngComm* 2011, **13**: 3878-3883.
- [23] Fujinami K, Katagiri K, Kamiya J, *et al.* Sub-10 nm strontium titanate nanocubes highly dispersed in non-polar organic solvents. *Nanoscale* 2010, **2**: 2080-2083.
- [24] Shevchenko EV, Talapin DV, Murray CB, *et al.* Structural characterization of self-assembled multifunctional binary nanoparticle superlattices. *J Am Chem Soc* 2006, **128**: 3620-3637.
- [25] Dong A, Chen J, Vora PM, *et al.* Binary nanocrystal superlattice membranes self-assembled at the liquid–air interface. *Nature* 2010, **466**: 474-477.
- [26] Luther JM, Law M, Song Q, *et al.* Structural, optical, and electrical properties of self-assembled films of PbSe nanocrystals treated with 1,2-Ethanedithiol. *ACS Nano* 2008, **2**: 271-280.
- [27] Cölfen H, Antonietti M. Mesocrystals: Inorganic superstructures made by highly parallel crystallization and controlled alignment. *Angew Chem Int Ed* 2005, **44**: 5576-5591.
- [28] Konstantatos G, Howard I, Fischer A, *et al.* Ultrasensitive solution-cast quantum dot photodetectors. *Nature* 2006, **442**: 180-183.
- [29] Luther JM, Law M, Beard MC, *et al.* Schottky solar cells based on colloidal nanocrystal films. *Nano Lett* 2008, **8**: 3488-3492.
- [30] Penn R, Banfield JF. Morphology development and crystal growth in nanocrystalline aggregates under hydrothermal conditions: Insights from titania. *Geochim Cosmochim Acta* 1999, **63**: 1549-1557.
- [31] Du N, Zhang H, Chen B, *et al.* Ligand-free self-assembly of ceria nanocrystals into nanorods by oriented attachment at low temperature. *J Phys Chem C* 2007, **111**: 12677-12680.
- [32] Pacholski C, Kornowski A, Weller H. Self-assembly of ZnO: From nanodots to nanorods. *Angew Chem Int Ed* 2002, **41**: 1188-1191.
- [33] Cölfen H, Mann S. Higher-order organization by mesoscale self-assembly and transformation of hybrid nanostructures. *Angew Chem Int Ed* 2003, **42**: 2350-2365.
- [34] Penn RL, Oskam G, Strathmann TJ, *et al.* Epitaxial assembly in aged colloids. *J Phys Chem B* 2001, **105**: 2177-2182.
- [35] Leunissen ME, Christova CG, Hynninen AP, *et al.* Ionic colloidal crystals of oppositely charged particles. *Nature* 2005, **437**: 235-240.
- [36] Shipway AN, Lahav M, Gabai R, *et al.* Investigations into the electrostatically induced aggregation of Au nanoparticles. *Langmuir* 2000, **16**: 8789-8795.
- [37] Tzeng SD, Lin KJ, Hu JC, *et al.* Templated self-assembly of colloidal nanoparticles controlled

- by electrostatic nanopatterning on a  $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$  electret. *Adv Mater* 2006, **18**: 1147-1151.
- [38] Chen KM, Jiang X, Kimerling LC, *et al.* Selective self-organization of colloids on patterned polyelectrolyte templates. *Langmuir* 2000, **16**: 7825-7834.
- [39] Shimooka H, Kohiki S, Kuwabara M. Characterization of barium titanate nanoparticles and dense nanograin free-standing films via sol-gel method using highly concentrated alkoxide solution. *J Ceram Soc Jpn* 2010, **118**: 674-678.
- [40] Burns G, Dacol FH. Glassy polarization behavior in ferroelectric compounds  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ . *Solid State Comm* 1983, **48**: 853-856.
- [41] Viehland D, Jang SJ, Cross LE. Local polar configurations in lead magnesium niobate relaxors. *J Appl Phys* 1991, **69**: 414-419.
- [42] Heywang W. Resistivity anomaly in doped barium titanate. *J Am Ceram Soc* 1964, **47**: 484-490.
- [43] Kuwabara M, Matsuda H, Hamamoto K. Giant piezoresistive effects in single grain boundaries of semi conducting barium titanate ceramics. *J Electroceram* 1999, **4**: 99-103.
- [44] Hamamoto K, Kuwabara M. Effect of electric-field-induced polarization on positive temperature coefficient of resistivity characteristics of semiconducting barium titanate ceramics. *Jpn J Appl Phys* 2001, **40**: L1163-L1165.
- [45] Choi KJ, Biegalski M, Li YL, *et al.* Enhancement of ferroelectricity in strained  $\text{BaTiO}_3$  thin films. *Science* 2004, **306**: 1005-1009.
- [46] Harrington SA, Zhai J, Denev S, *et al.* Thick lead-free ferroelectric films with high Curie temperatures through nanocomposite induced strain. *Nature Nanotech* 2011, **6**: 491-495.
- [47] Haeni JH, Irvin P, Chang W, *et al.* Room-temperature ferroelectricity in strained  $\text{SrTiO}_3$ . *Nature* 2004, **430**: 758-761.
- [48] Xiong Y, Xia Y. Shape-controlled synthesis of metal nanostructures: The case of palladium. *Adv Mater* 2007, **19**: 3385-3391.