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A New Trend of Ceramics Research in Japan: ''Frontier Ceramics'' National Project

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Abstract. This paper describes a new concept thrust in advanced ceramics entitled ''Frontier Ceramics.'' A national project concerning Frontier Ceramics was organized by the Ministry of the Science Technology Agency of Japan. The key objective of the program is to provide an improved understanding of boundaries or interfaces. The approach to be taken is to develop improved means for tailoring ceramic interface through control of structure and composition by use of novel processing techniques and thereby to achieve desired properties. Three main topics in the project relate to the construction of (1) ''singular point model'', (2) ''ordering interface model,'' and (3) ''continuous interface model.'' Some recent results using bicrystals were reviewed.

Keywords: frontier ceramics, interface, grain boundary, bicrystals, microstructure

1. Needs and Objects for Frontier Ceramics

The key objectives of any ceramic materials R & D are to improve the manufacturing processes, to achieve higher performance of the existing ceramics, to introduce novel functions and/or to create new materials. Materials with excellent performance and novel functions are likely to lead to new and improved technologies in the future [1]. The ''Frontier Ceramics'' Project (hereafter, denoted Froc) has this as one of its key objectives. The basic concepts for Froc are indicated in Table 1. Frontier ceramics are considered to be one of the ''post-advanced ceramics.'' A materials science committee under the ministry of the Science and Technology Agency in Japan selected interfacial science in ceramics materials as an important field for study. Following a feasibility study in 1994, Froc was initiated and organized on a five-year basis in 1995. Nineteen university, industry and government research institutes or laboratories are participating in this project. This report concentrates on Froc concepts and recent studies.

Few electronic applications can be constructed without ceramic components. Ceramics, therefore, require development in parallel with advances of electronic devices. One major trend in device development is towards greater miniaturization of the device size. Similar trends are in evidence in ceramic device development. The ceramic capacitor is a typical example as can be seen from Fig. 1. Aggregates of grains are characteristic of the conventional ceramics. In the miniaturization of ceramic capacitor, this characteristic is being challenged. Reducing the grain boundary area may be one way to attack the down sizing objective. Structures with few grains between internal electrode have already been realized. One goal of future ceramics is to construct them with a single grain boundary or without grain boundaries. In such a case ''an averaging effect'' would not determine the stability of the properties. For devices which depend on grain boundaries or interphase boundary characteristics, such as PTC, varistors etc., individual interfaces must be controlled. Due to these stringent requirements, the

Table 1. Comparison of ''Frontier Ceramics'' with conventional ceramics

	Raw materials	Processing	Phases	Interfacial chemical composition	Interfacial structure	Origin of properties
Traditional ceramics	Natural products	(Liquid-phase) sintering	Many and complicated phases, uncontrollable	Uncontrollable	Uncontrollable	Bulk characteristics.
Advanced ceramics	Artificial materials	(Liquid-phase and solid-phase) sintering	Relatively small number of phases, partially controllable	Partially controllable.	Statistical variation, partially controllable	Mainly bulk characteristics
Frontier ceramics	**Artificial materials**	**Sintering + advanced processing (sputtering, MBE, etc.)**	**A few and simple phases, precisely controllable**	**Design and precise control**	**Design and precise control**	**Mainly interfacial characteristics**

Froc national project is focusing its attention on the design of the structure and composition of ceramic interfaces and towards the establishment of the relationships between the designed interface and the function of the ceramic as a whole. A unifying model of grain boundary behavior will be the objective of phase two of this research. Similar needs are widely seen for research and development of related areas of ceramics, electrodes, catalysis, engineering ceramics, and so on.

2. Fundamental Concepts for Modeling Interface

The materials science of ceramics deals with many issues relating to interfaces including surface [2]. To characterize the various interfaces investigated in Froc, we grouped them into three classes of interface models, i.e., the first is the ''singular point model,'' second, the ''ordering interface model,'' and the last, the ''continuous interface model.'' These funda-

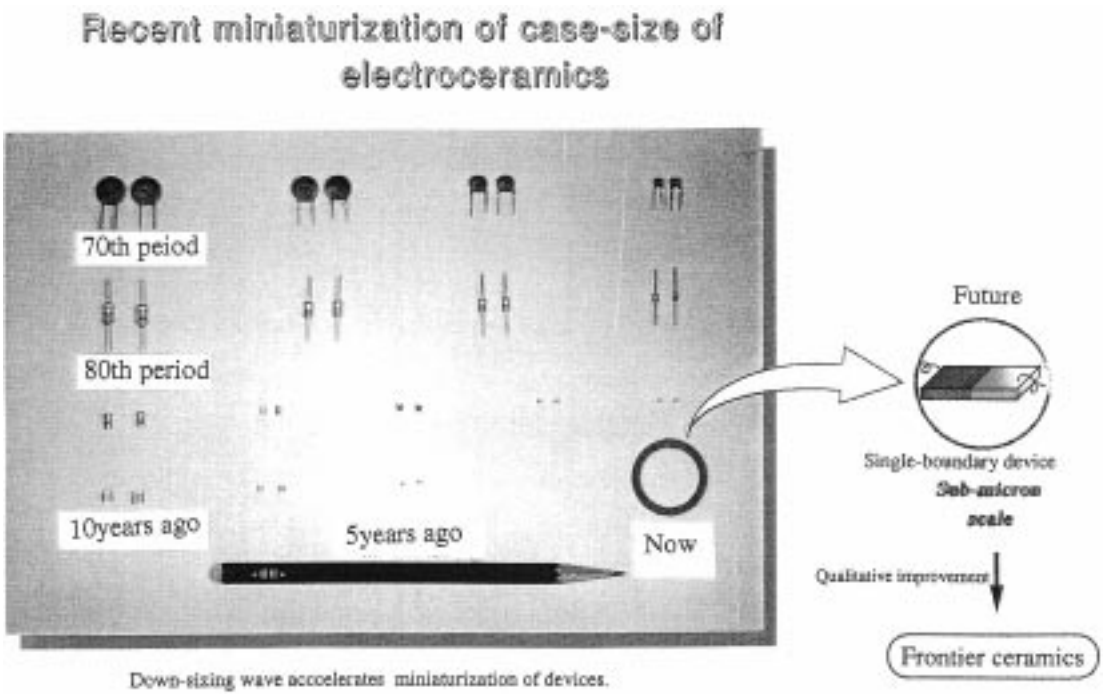

Fig. 1. Recent down-sizing of capacitors.

mental concepts are shown in Fig. 2. Each model is appropriate for special dimensions.

For the first model, ''singular point'' refers to point defect, impurities or aggregates of these defects. These are largely on the scale of under 0.1 nm. Localized energy state models such as molecular orbital theory, therefore, apply logically on this scale [3]. As an example, Fig. 3 shows electron density maps of a strontium titanate surface, calculated by the DVX_{α} method [4]. According to these results, titanium ions neighboring oxygen vacancies exhibit the trivalent state.

In the ''ordering interface model'', one considers mainly the 1–10 nm region neighboring the interfaces. In this case, the interface is commonly modeled as an interface with periodic structure, such as the ''coincident site lattice (CSL)'' [5]. Assuming an ordered structure, band theory and the molecular dynamics can be applied. Koyama clarified stable configurations and electronic distributions for SiC-Al interfaces and grain boundaries in SiC ($\{122\}$ $\Sigma = 9$ boundary) by using first-principles molecular dynamics [6, 7]. Figure 4 shows a typical treatment of a stable structure and electron distribution in SiC [6].

Finally in the ''continuous interface model,'' the various studies are carried out on the scale of 10–100 nm where one views the interface a continues phase. The relations between the compositional distribution near interface and properties are investigated [8]. In this regime it is noted how the thermodynamics with macro quantities such as chemical potential is applied to very small dimension.

The characteristics of ceramic interfaces are not simply physical in nature but are strongly influenced as well by the chemical aspects. Chemical reactions at the interfaces are particularly important at interfaces used for catalysis, sensors and electrode materials. , i.e., the interfaces give a reaction fields to chemical reaction systems (here, called ''functional frontier'').

''Molecular-recognizing sensor'' and catalysis controlled by an external field are illustrated in Fig. 5. Two inverse processes are at work. In the former the physical signal such as the electric field or current results from a chemical reaction at interface while in the latter the interfacial chemical reaction is controlled by a physical field. In these materials, a conversion between ''chemical paths'' and ''physical paths'' at interface are utilized.

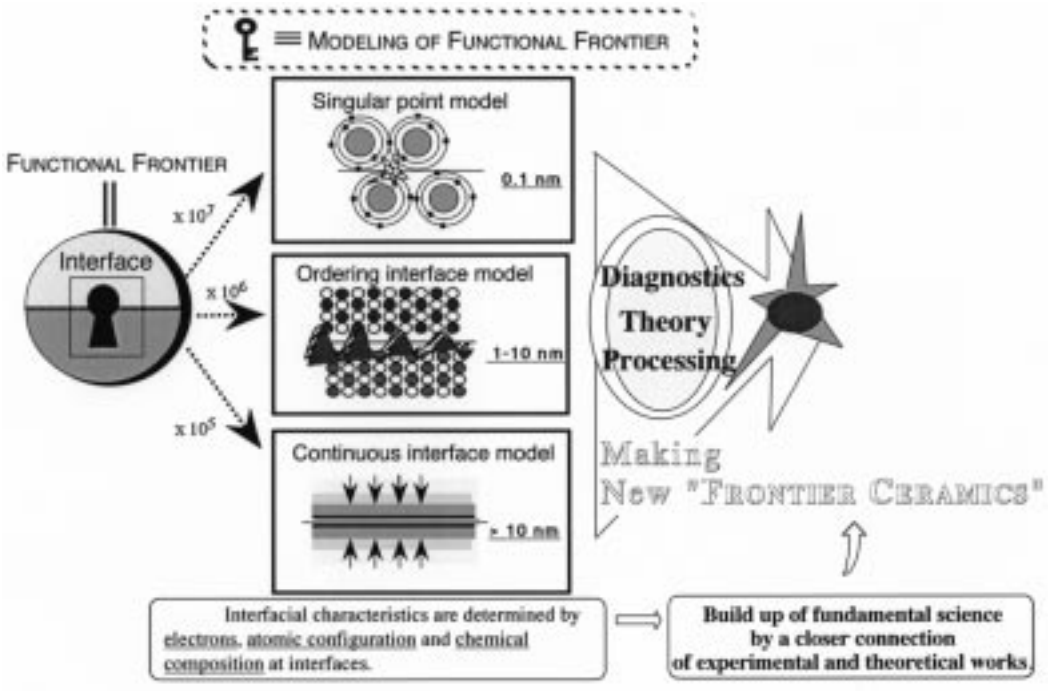

Fig. 2. Concepts for making the new ''Frontier Ceramics'' and three kinds of interface-models. Interficial phenomenon, understood from atomistic order to mezoscopic order.

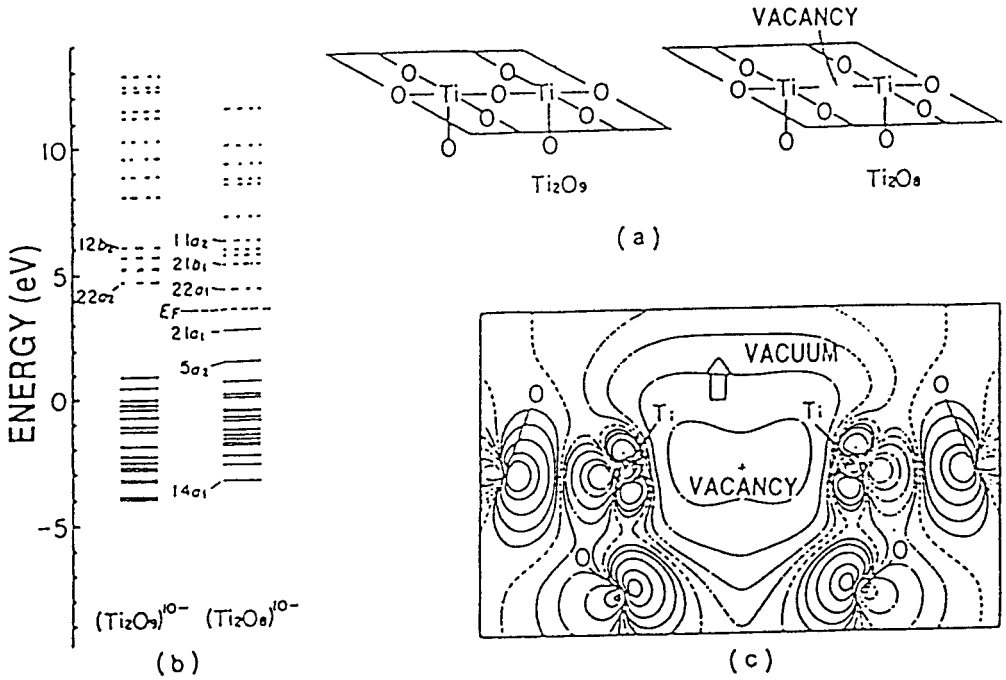

Fig. 3. (a) Model clusters of (100) surface of $SrTiO_3$ with/without O-vacancy. (b) Their energy level diagrams. (c) A contour map of $21a_1$ MO in the $(Ti_2O_8)^{10-}$ cluster on *xz* plane.

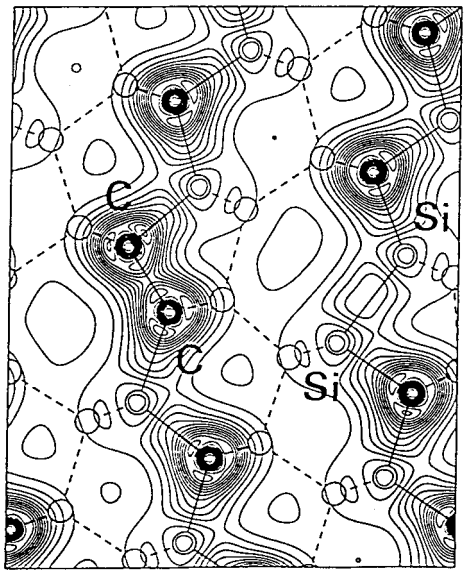

Fig. 4. Relaxed configurations of {122} $\Sigma = 9$ boundary in SiC. Contours of the valence electron density plotted from 0.010 to 0.270 in spacing of 0.020 in atomic units. Circles, and solid lines, indicate the atomic positions and bonds on the (011) plane, respectively [6].

3. Recent Research of Frontier Ceramics Project

Single grain boundaries provide the optimum structure for application of the type of modeling described above. We focus, in this section, on methods for preparing such single boundaries.

One approach has been the fabrication of fibers of PTC barium titanate. The fiber consists of a chain of many single crystal grains. Although the control of the crystal direction of each grain is difficult, it allows the treatment of many single boundaries in series at once. Understanding of the anisotropy of the PTCR effect is also being promoted, as a result of measurement of PTC characteristics at each boundary.

Several groups are trying to apply thin film techniques or ion implantation methods for making single grain boundaries. One can not choose some orientation in boundaries, but it can be possible to obtained desired compositions. Using this method, zinc oxide thin film varistor was created.

Bicrystals formed by sintering individual single crystals together are being used for measurement of

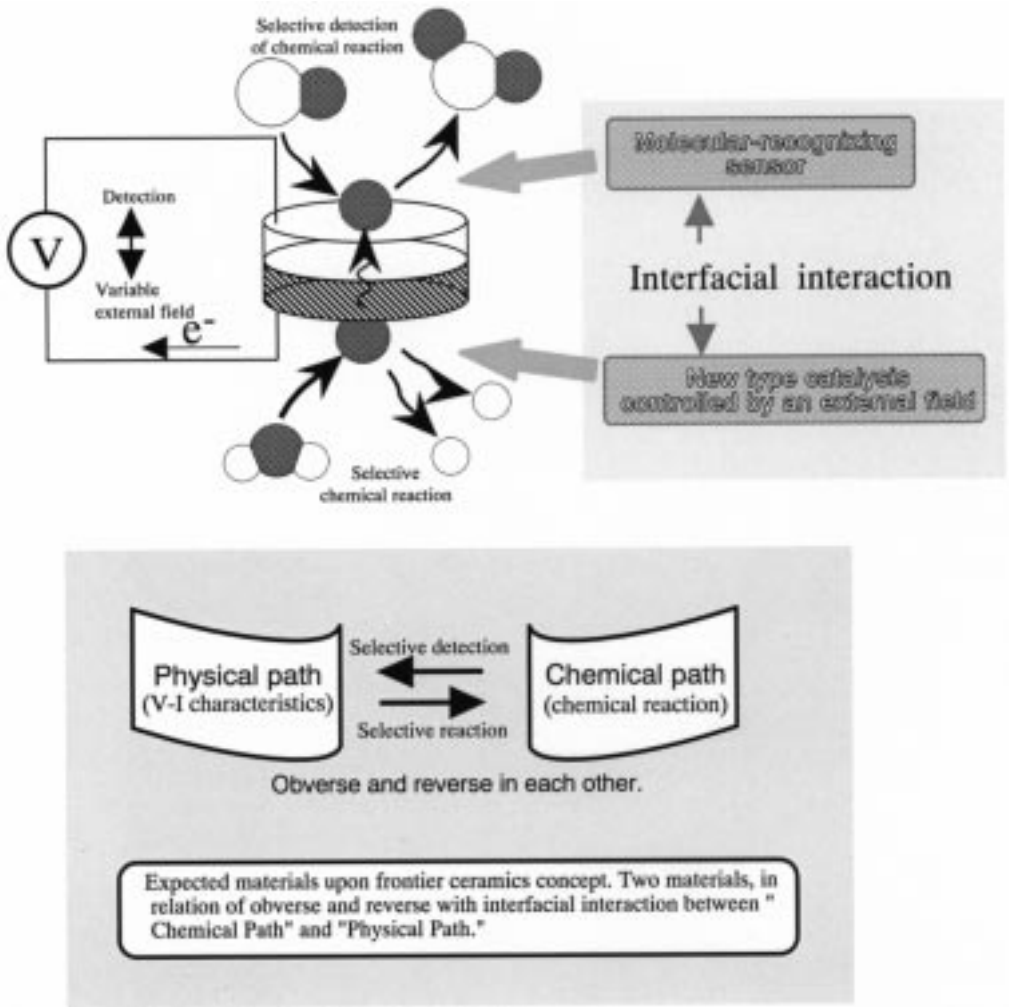

Fig. 5. Expected materials bases upon the frontier ceramic concept. Interfacial interactions corresponding to a ''chemical path'' and ''physical path.'' See text for discussion.

electrical properties. This enables the choice of orientation and composition at boundary. Here, we report characteristics of single boundaries of strontium titanate joined by hot isostatic pressing. It is well known that $SrTiO_3$ semiconductor ceramics doped with lanthanum or niobium are used for capacitors and varistors. These functions are obtained by post-annealing in air and forming an insulating layer at grain boundaries after initially sintering in reducing atmosphere. However, the mechanism controlling the non-linear electrical effects is not yet clear due to a lack of information regarding grain boundary anisotropy, local composition, etc. Modeling will be helpful in clarifying these phenomena.

Figure 6 shows the relation between the twist angle of a strontium titanate bicrystal and the electrical non-linearity [9]. The degree of non-linearity is clearly increasing with angle which relates to the structural irregularity at the boundary. The same tendency was observed for tilt boundaries. In polycrystalline materials, the addition of bismuth results in segregation at grain boundaries and an increase in nonlinearity. Bismuth-implanted samples exhibited higher non-linearities than non-modified sample [10]. These facts suggest that the structure of model boundaries must be established and point defects such as impurities, considered to be the origin of boundary states, must be characterized.

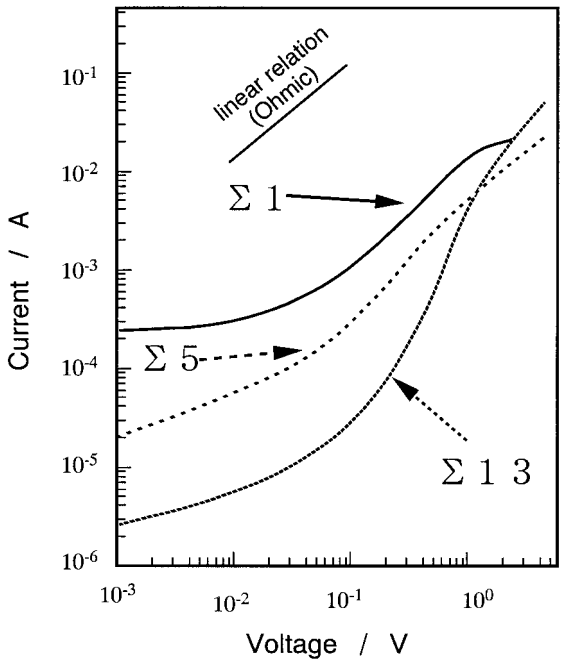

Fig. 6. Relation between twist angle and *I-V* characteristics in Nb-doped $SrTiO_3$ bicrystals. Electrical non-linearity increases with twist angle.

The most striking characteristic of internal boundaries is their lack of direct access in contrast to surfaces. This feature has limited progress in interfacial science. STM, very useful in structural studies of surface, can not be readily applied to the internal boundaries. On the contrary TEM is the best method for the studies of structural problems at boundaries. Although TEM analysis is essentially destructive, atomic order analysis near grain boundaries is possible and ion configurations can be visualized. In the Froc program, two groups are active in this field. One group is examining grain boundary structure in relation to magnetic permeability in a ferrite and ferroelectric transition in strontium calcium titanate ceramics [11]. Another group is studying stability of structures at hetero-interface, comparing to the theoretical results [12].

Because boundaries typically exhibit larger free volumes than the bulk, the interface provides space for chemical reactions and interaction (function frontier) as mentioned above. These also serve as ''pipes'' for the enhanced movement of chemical species, i.e., boundary diffusion. The anisotropy of diffusion has been little studied in ceramic materials. Two groups are studying this problem in the Froc

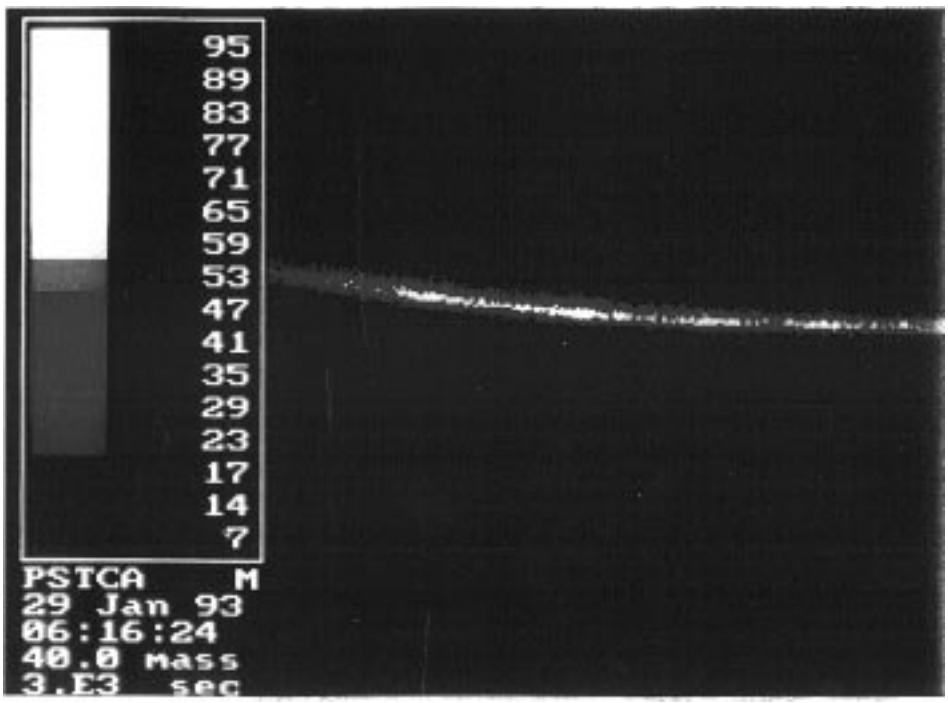

Fig. 7. Oxygen-18 diffusion along single grainboundary with low twist angle in Nb-doped $SrTiO_3$ bicrystals.

program. A typical result of diffusion in a bicrystal of strontium titanate is shown in Fig. 7, where it appears that oxygen ions preferentially diffuse along single boundary [13]. The twist angle of this grain boundary was less than a few degrees, and the boundaries did not exhibit varistor characteristic. Furthermore, it is experimentally observed that oxygen vacancies annihilated at this kind of boundary.

We reviewed some results for single grain boundaries. In the future, new models will be proposed, and new materials will be found, combining these results. We believe that the understanding of actual and typically more complex boundaries will progress, as a result of the Froc program.

4. Summary

The ''Frontier Ceramic'' Project (Froc) was organized under the Ministry of the Science and Technology Agency in Japan. Froc focuses on the study of interfaces and grain boundaries, with the first objective, the establishment of models for the boundaries. These include molecular orbital theory, band calculations, and a non-equilibrium thermodynamics calculations as one of the main themes. Recent results, using bicrystals were reviewed. Progress in the basic science of the grain boundaries, we believed, will lead to improved performances of grain boundary and controlled devices, and to new materials.

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