

# Cation Doping of Oxide Ceramics Using Solid Oxide Electrochemical Doping: Evaluation of the SOED 2 Method

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Electrochemical cation doping into oxide ceramics has been carried out using the solid oxide electrochemical doping (SOED 2, electro-bi-injection) method. The SOED 2 method consists of the anode(Ag)/ $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub>/ceramics/YSZ/cathode(Pt) electrolysis system, where the metal cation  $M$  and oxygen anion are simultaneously injected into the oxide ceramics so that electrical neutrality is maintained in the ceramics. Ceramics of three kinds of oxides with different conductive properties (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>, Fe<sub>2</sub>O<sub>3</sub>, and BaTiO<sub>3</sub>) were studied in doping experiments. In general, graded doping occurred independent of the conductivity type of the oxide ceramics at relatively high temperature because the migration rate of the oxygen anions is close to that of the metal cation in the grain boundaries of the ceramics at high temperature. As a result, the metal cation was graded on the anode side of the oxide ceramics. However, doping is too difficult at low temperature because the migration of oxygen anions is much faster than that of the cations at low temperature. As expected, doping results depended on the valence of the doped cation. The doping mechanism is discussed in detail. © 1999 Academic Press

## INTRODUCTION

The physical and chemical properties of ceramics depend significantly on the kind of cations doped in the lattice. Therefore, the cation doping into the ceramics is very important for the development of functional ceramics. We have developed a new electrochemical doping method using  $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub> as a solid electrolyte which is called the solid oxide electrochemical doping (SOED) method where only the cation moves in the ceramics because  $\beta''$ -Al<sub>2</sub>O<sub>3</sub> blocks the movement of the electron, hole, and oxygen anion. The SOED method has merits such as grain boundary selective doping, controlling the amount of the dopant by the electric charge, etc., compared with conventional doping methods. In particular, this will be a very useful method for microarea doping if the tip of the solid electrolyte is used during the electrolysis. Moreover, the graded materials in the dopants

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(for example, optical glass materials, etc.) can easily be made with the SOED methods when the doping time is very short (for example, by a pulse electrolysis technique). These techniques are very important for the development of the electroceramics used in microelectronics and are impossible by the previously stated conventional method.

There are two main systems in the SOED method. One is the SOED 1 system where the  $M$  cation in  $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub> is substituted for the metal cation in the ceramics ((a) in Fig. 1). The other is the SOED 2 system where the  $M$  cation in  $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub> is injected into the ceramics together with an oxygen anion ((b) in Fig. 1). The mechanism in the latter system has not been studied previously, although the electrosubstitution mechanism of the SOED 1 system has been proposed in discussions of the SOED 1 system (1–4). The purpose in this study is to evaluate the SOED 2 system as a doping method and to clarify the mechanism.

## EXPERIMENTAL

Experiments were carried out using oxides including the superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> (YBCO, Dowa Kogyo Co.), the semiconductor Fe<sub>2</sub>O<sub>3</sub> (Nacalai Tesque Co.), and the insulator BaTiO<sub>3</sub> (Fuji Titanium Co.) as the doping target. The sintering pellet samples (thickness, 1.5 mm; surface area, 0.6 cm<sup>2</sup>) of each of these oxides were prepared by pressing the powders under 1000 kg/cm<sup>2</sup> and heating at 930–1300°C. The cation conductors,  $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub>, were prepared by substitution of  $M$  for Na in Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, where the Na- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> (Nihon Tokushu Togyo Co.) polycrystal pellet was immersed in the appropriate molten salt consisting of  $M$  as previously reported (5–7). Y-stabilized ZrO<sub>2</sub> (YSZ, 8 mol% Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, Nikkato Co.) was used as an oxygen anion conductor in the SOED 2 system. The apparent contact area in the  $M-\beta''$ -Al<sub>2</sub>O<sub>3</sub>/ceramics was 0.2 cm<sup>2</sup>. Good contact in the ceramic/ceramic interfaces which avoids the current inhomogeneities has been achieved by rubbing the ceramics strongly against each other. Electrolysis was carried out for 3 h under a constant current density at 400 or 600°C. No cation doping occurred in the absence of bias at

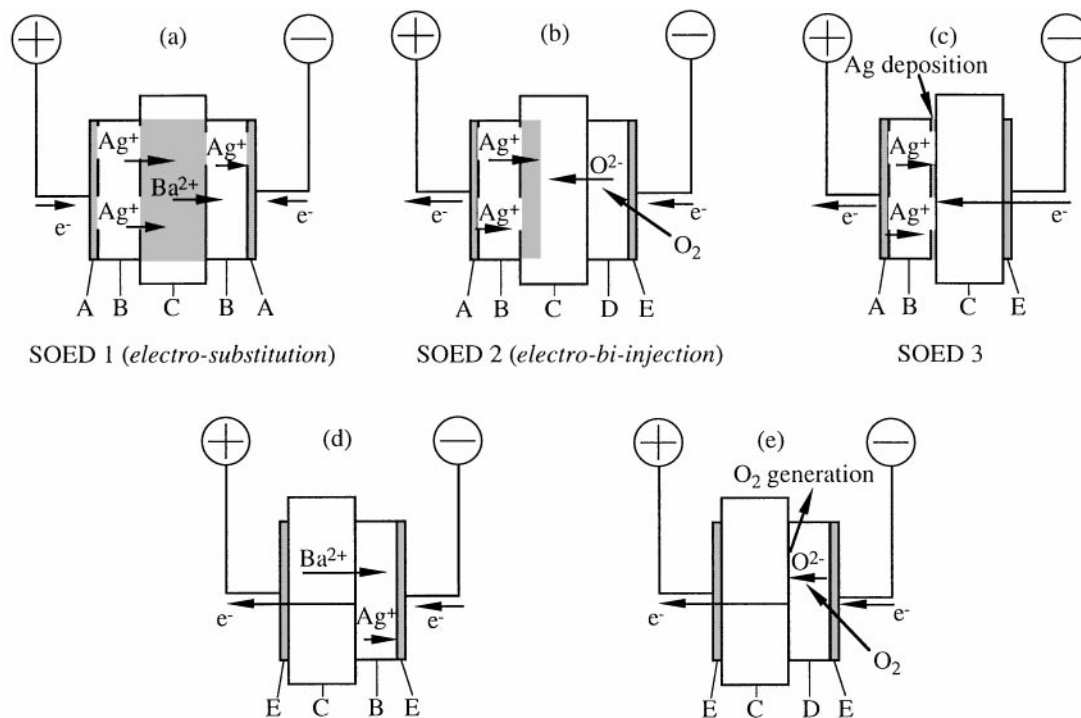
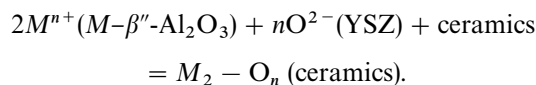


FIG. 1. Models of the ion migration for various SOED methods. A, Ag; B, Ag- $\beta''$ -Al<sub>2</sub>O<sub>3</sub>; C, ceramics; D, YSZ; E, Pt.

these temperatures. After the electrolysis, the elemental distribution of the dopant in a cross section of the doped ceramics was measured using electron probe microanalysis (EPMA). The crystal structure of the samples was analyzed from the X-ray diffraction (XRD) patterns.

## RESULTS AND DISCUSSION

The basic migration mechanism in the present SOED 2 system for the Ag<sup>+</sup> doping into YBCO is illustrated in Fig. 1b. Ag is electrochemically oxidized to Ag<sup>+</sup> at the interface of Ag/Ag- $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, and then Ag<sup>+</sup> in Ag- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> is injected into the oxide ceramics. Oxygen in the air is electrochemically reduced to O<sup>2-</sup> at the YSZ/Pt interface, and O<sup>2-</sup> is injected into the oxide ceramics. Therefore, this doping scheme corresponds to "electro-bi-injection." The following overall reaction in the SOED 2 system will occur in the ceramics together with the electrochemical reactions at the anode (oxidation of metal into cation) and cathode (O<sub>2</sub> reduction into O<sup>2-</sup>):



Experimental results for doping with various cations by the SOED 2 system are listed in Table 1. Two doping types,

A and B, are represented in this table. Type A corresponds to a graded doping at the anode side of the ceramic sample while type B corresponding to uniform doping over the entire ceramic sample. A third type (type C) corresponds to no doping but the metal or oxide was deposited at the anode side interface of the M- $\beta''$ -Al<sub>2</sub>O<sub>3</sub>/ceramics. The results in this table indicate that various cations can be doped into the oxide ceramics at high temperature and that facile doping is observed for monovalent cations (Ag<sup>+</sup>, Na<sup>+</sup>) compared with the divalent cations (Sr<sup>2+</sup>, Ca<sup>2+</sup>) because monovalent cations were doped at relative low temperature as listed in Table 1. These results demonstrate that the SOED 2 system is very useful for doping into all of the oxide ceramics, i.e., YBCO, BaTiO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>, independent of their conductive properties but dependent on the electrolysis temperature.

Figure 2 shows typical EPMA distribution line scans of the elements in a cross section of the YBCO sample doped with Ag<sup>+</sup> under 5 mA/cm<sup>2</sup> at 600°C using the SOED 2 system. The Ag dopant was distributed on the anode side of the YBCO ceramics (type A doping). Thus, the graded doping was a general characteristic of the SOED 2 system. Ag was uniformly doped over the entire YBCO sample when the doping was carried out using the SOED 1 system under the same electrolysis condition as previously reported (1). In this case, only Ba was detected in the cathode side Ag- $\beta''$ -Al<sub>2</sub>O<sub>3</sub> according to the EPMA analysis. On one hand, this

**TABLE 1**  
**Experimental Results in the SOED 2 Method**

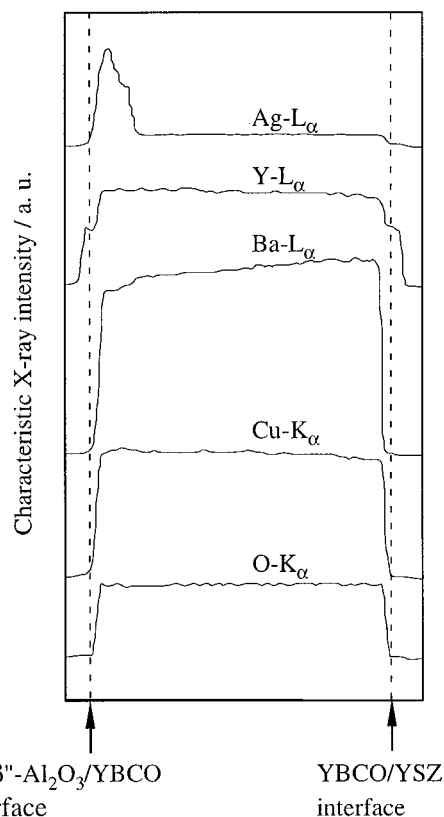
Ceramics	Current density (mA/cm <sup>2</sup> )	Doping cation	Electrolysis temperature (°C)	Doping type <sup>a,b</sup>	
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>y</sub>	5	Ag <sup>+</sup>	400	A	
			600	A	
	0.5	Na <sup>+</sup>	400	B	
			600	B	
		Sr <sup>2+</sup>	400	C	
			600	A	
0.5	Ca <sup>2+</sup>	400	C		
		600	A		
	BaTiO <sub>3</sub>	0.5	Ag <sup>+</sup>	400	C
			Sr <sup>2+</sup>	400	C
			600	A	
Fe <sub>2</sub> O <sub>3</sub>	0.5	Ag <sup>+</sup>	400	A	
			600	A	
		Sr <sup>2+</sup>	400	C	
			600	A	

<sup>a</sup>Main doping point of the all dopants is the grain boundaries in the ceramics.

<sup>b</sup>Doping types A, B, and C correspond to the graded doping at the anode side of the ceramics, doping over the entire sample, and metal or oxide deposition at the anode side interface of *M*-β''-Al<sub>2</sub>O<sub>3</sub>/ceramics, respectively.

indicates that only the Ba<sup>2+</sup> ion is released from the YBCO ceramics under an electrical force so that the electrical neutrality is maintained in the ceramics as shown in Fig. 1a. On the other hand, no Ag doping into the YBCO occurred, but Ag metal was deposited at the Ag-β''-Al<sub>2</sub>O<sub>3</sub>/YBCO interface when the SOED 3 system ((c) in Fig. 1) was used. The oxygen anion will not be doped into the YBCO using the electrolysis system (e), but O<sub>2</sub> will be generated at the YBCO/YSZ interface (see (e)) as stated below. From these results, it was judged that the electrochemical cation doping did not occur when electrical neutrality was not maintained in the ceramics. Thus, the injection of the oxygen anion is very important for the cation doping in the SOED 2 system.

Figure 3 shows the dependence of the applied voltage on the electrolysis time for a constant current density (5 mA/cm<sup>2</sup>) at 600°C. Figures 3a–3e correspond to the electrolysis systems shown in Figs. 1a–1e, respectively. The applied voltage in (b) was lower than that in (a) during the initial stage of the electrolysis, but abruptly increased with the electrolysis time at 90 min. In the SOED 1 system (a), a large voltage will be mainly based on the applied voltage for the Ba<sup>2+</sup> migration through the YBCO ceramics (1). The large applied voltage for the electrolysis system (d) indicates that the direct injection of Ba<sup>2+</sup> from the YBCO into Ag-β''-Al<sub>2</sub>O<sub>3</sub> is difficult. For the electrolysis systems (c) and (e), their applied voltages were small compared with those of



**FIG. 2.** EPMA elemental distribution line scans in the cross section of the YBCO doped with an Ag sample at 600°C by the SOED 2 system.

the other systems and were close to the voltages calculated from both ionic conductivities of Ag<sup>+</sup> and O<sup>2-</sup> in Ag-β''-Al<sub>2</sub>O<sub>3</sub> and YSZ, respectively. This indicates that no doping of these ions into the YBCO ceramics occurs. Consequently, the following phenomena will occur in the SOED 2 system. Initially, both Ag<sup>+</sup> and O<sup>2-</sup> ions are smoothly injected into the YBCO ceramics until the amount of the Ag<sup>+</sup> doped into the anode side of the YBCO saturates (<90 min in (b)). The applied voltage is not so large in this stage. After the saturation, the Ag<sup>+</sup> will be difficult to migrate in the ceramics where the applied voltage increases with the electrolysis time (>90 min in (b)). In fact, both distribution states of the Ag dopant (graded doping) after 90 and 180 min of electrolysis were similar to each other, according to the EPMA analysis.

An X-ray qualitative analysis was carried out in some sections of the YBCO sample doped with Ag at 600°C by the SOED 2 system. Two micropoints were analyzed in the cross section of the doped sample. One is the area analysis which corresponds to all parts of the doped sample, i.e., grain bulk and grain boundaries in the sample. The other is a pinpoint analysis to detect the elements only in the grain bulk. The peak attributed to Ag was observed only in the area analysis. This indicates that Ag was selectively doped

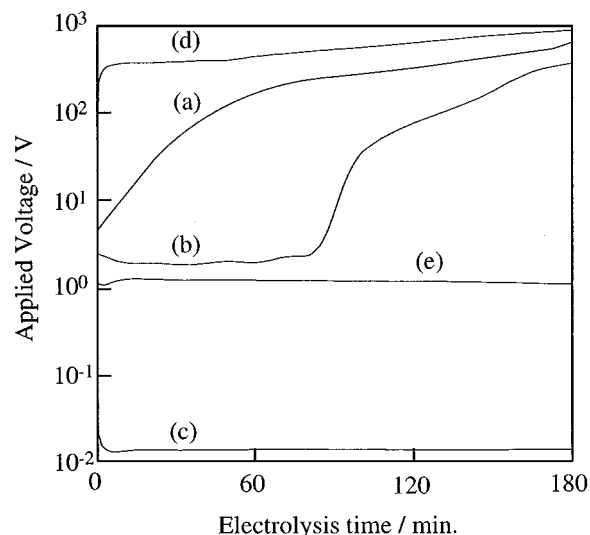


FIG. 3. Dependence of the applied voltage on the electrolysis time under  $5 \text{ mA/cm}^2$ . (a)–(e) corresponds to those for the electrolysis systems given in Fig. 1, respectively.

only in the grain boundaries. Thus, both Ag and oxygen migrate more smoothly in the grain boundaries than in the bulk. Other cations such as  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ , and  $\text{Ca}^{2+}$  were also doped into the grain boundaries. Thus, the SOED 2 method is very useful for selective doping in the grain boundaries.

Composition and lattice parameters of both contact surfaces in the Ag-doped YBCO sample prepared by the SOED 2 system were analyzed from XRD patterns. Only a small amount of impurities such as  $\text{BaCO}_3$ ,  $\text{CuO}$ , and Ag metal were detected on the anode side surface, while no change was observed on the cathode side surface. In

principle, the cation doping using the SOED 2 system will proceed without any destruction of the crystal since the doping occurs only in the grain boundaries without cation exchange. In fact, no change in the lattice parameters of the doped YBCO was observed. Therefore, the SOED 2 system may be more useful than the SOED 1 system (electrosubstitution) when the substitution of the dopant cation is difficult in the ceramics (4).

The electrolysis temperature is very important for doping using the SOED 2 system. Figure 4 shows two EPMA distribution line scans of the elements in the Sr-doped  $\text{BaTiO}_3$  ceramics under  $0.5 \text{ mA/cm}^2$  at 400 and 600°C. On one hand, Sr was not doped into the  $\text{BaTiO}_3$  but deposited at the  $\beta''\text{-Al}_2\text{O}_3/\text{BaTiO}_3$  anode interface as SrO at 400°C. On the other hand, Sr was doped into the  $\text{BaTiO}_3$  ceramics at 600°C as the figure shows (graded doping). The same phenomena were also observed for the cases of the Sr and Ca doping into the YBCO, the Ag doping into the  $\text{BaTiO}_3$ , and the Sr doping into the  $\text{Fe}_2\text{O}_3$ , as listed in Table 1. In these cases, Ag, Sr, and Ca were deposited as a metal or oxide at the anode side interfaces at 400°C, analogous to Fig. 4 (400°C). In the SOED 2 system, the doping will be determined by the degree of the migration rates of the cation dopant and the oxygen anion in the grain boundaries. It is well-known that the diffusion rate of the oxygen anion through the oxide ceramics is much larger than that of the metal cation. Therefore, cation doping will be generally difficult at low temperature. Both migration rates of the cation dopant and the oxygen anion will come close to each other at high temperature because the activation energy of the cation diffusion through the oxide ceramics is larger than that of the oxygen anion. For example, activation energies of the  $\text{Ag}^+$  and oxygen anion diffusion through the YBCO ceramics are 2.2 and 1.5 eV, respectively (8, 9).

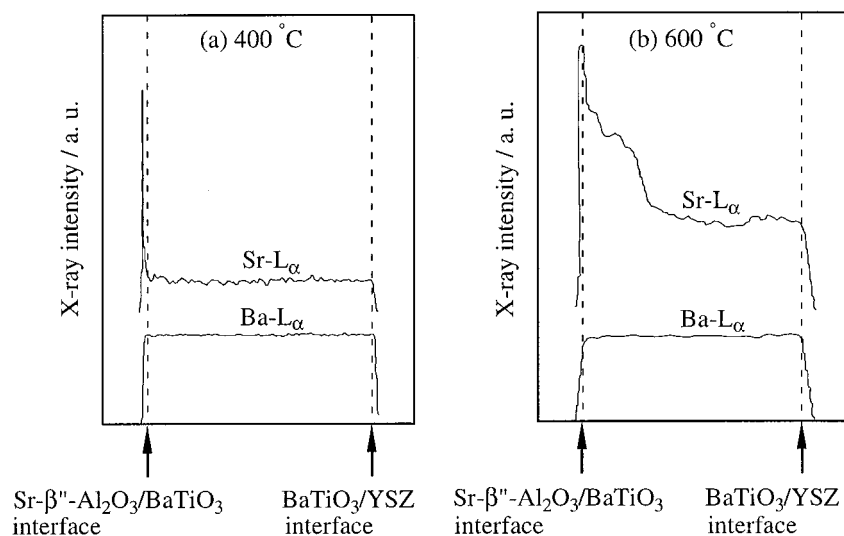


FIG. 4. EPMA elemental line scans for the  $\text{BaTiO}_3$  ceramics doped with Sr by the SOED 2 system.

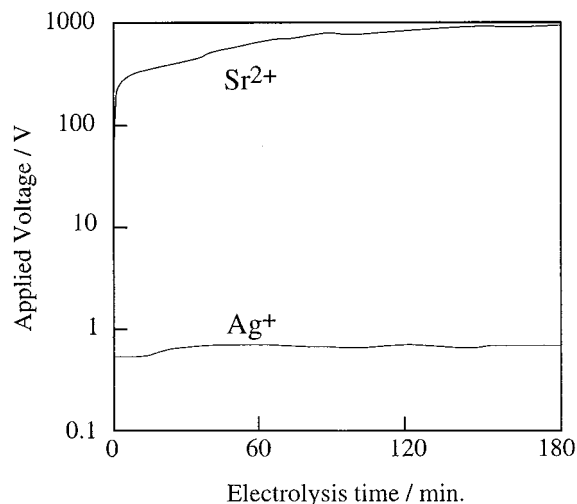


FIG. 5. Dependence of the applied voltage on the electrolysis time under  $0.5 \text{ mA/cm}^2$  for the Ag and Sr doping into the  $\text{Fe}_2\text{O}_3$  at  $600^\circ\text{C}$  in the SOED 2 system.

Consequently, the cation doping into the oxide ceramics occurs easily at relatively high temperatures for the SOED 2 system.

Doping by the SOED 2 system also depends on the valence of the dopant cation as already stated. For the Ag and Sr doping into the  $\text{Fe}_2\text{O}_3$ , the monovalent cation ( $\text{Ag}^+$ ) can be easily doped into the  $\text{Fe}_2\text{O}_3$  at both  $400$  and  $600^\circ\text{C}$ , while the divalent cation ( $\text{Sr}^{2+}$ ) can be doped at  $600^\circ\text{C}$  but not at  $400^\circ\text{C}$  (Table 1). Figure 5 shows the dependence of the applied voltage on the electrolysis time under  $0.5 \text{ mA/cm}^2$  for the Ag and Sr doping into the  $\text{Fe}_2\text{O}_3$  at  $600^\circ\text{C}$ . The applied voltage can somewhat reflect the degree of the migration rate and will be small when the migration rate is large. The applied voltage for the case of  $\text{Sr}^{2+}$  was about 3 orders of magnitude larger than that for the case of  $\text{Ag}^+$  and reached about  $10^3 \text{ V}$  after 180 min. In general, the ionic conductivity of the metal cation in the oxide ceramics depends on its valence. For example, the ionic conductivity of the monovalent cation in the  $M-\beta''\text{-Al}_2\text{O}_3$  is higher than that of the divalent one (10) because the divalent cation is more significantly affected than the monovalent cation by electrostatic interaction from the oxygen lattice of the spinel structure in the  $M-\beta''\text{-Al}_2\text{O}_3$ . The Na doping into the YBCO is very easily compared with the case of the Ag doping since the former doping corresponds to type B but the latter corresponds to type A (Table 1). This difference can also be explained from the degree in the migration rate. The ionic conductivity is higher for  $\text{Na}^+$  than for  $\text{Ag}^+$  in the

$M-\beta''\text{-Al}_2\text{O}_3$  (10), although it seems to depend on the structure of the oxide ceramics to be doped.

The SOED 2 system gave an important possibility of the preparation for the graded materials in the application. The graded state of the dopant can be easily controlled by the electrolysis temperature, electrolysis time, and electrolysis current density. For example, an improvement of some thermoelectric materials can be achieved by the graded doping using SOED 2 method. This study, therefore, is in progress.

## CONCLUSIONS

Electrochemical cation doping into various oxide ceramics together with the injection of the oxygen anion was carried out using the SOED 2 method. The following important information was obtained and a doping mechanism was proposed.

1. The cation doping easily occurred together with the oxygen anion injection so that electrical neutrality was maintained in the ceramics.
2. Various cations were easily doped into the grain boundaries of the oxide ceramics at relatively high temperature. This will be based on the higher activation energy for the cation migration than for the oxygen anion migration in the grain boundaries of the oxide ceramics.
3. The graded doping at the anode side of the oxide ceramics generally occurred for the SOED 2 system. This will be based on the faster migration for the oxygen anion than for the dopant cation.
4. The doping was easier for the monovalent cation than for divalent cation. This tendency was in harmony with the degree of the cation migration rate in the  $M-\beta''\text{-Al}_2\text{O}_3$ .

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