

Ceramic Materials having Strain Sensing Properties - The CaO-NiO Ceramics -

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The strain sensing properties of the system $x\text{NiO}-(1-x)\text{CaO}$ with various compositions ($x=0.001-0.05$) are evaluated and the origin of the phenomena is guessed. We have found out that the high temperature electrical conductivity of the $x\text{NiO}-(1-x)\text{CaO}$ increases by applying the compressive stress at 1000°C . When the applied load is removed, the electrical conductivity rapidly decreases and returns to the original value, but a small hysteresis of the stress-conductivity curve is observed. After the loading test, the lattice parameter of the specimen is found lengthened. The correlation between the lengthening of the lattice parameter and the increase in the electrical conductivity by loading is discussed. The amount of the "expanded type" $\text{Ni}(\text{II})\text{O}_6$ clusters in the $x\text{NiO}-(1-x)\text{CaO}$ grains is supposed to be increased by the applied stress, which would be the origin of the strain dependent electric conduction in the $x\text{NiO}-(1-x)\text{CaO}$ system.

Key words : NiO-CaO solid solution, Electrical conductivity, Strain sensing, Weak ligand-field

I. Introduction

If the stress is applied to a ceramic material and the magnitude of the applied stress is sufficiently low, the material deforms elastically. When more stress is applied and the elastic energy exceeds the critical value, micro-cracks are suddenly produced and the fracture of the material proceeds at a stretch. If the elastic deformation could be monitored or detected easily, we could obtain a reliable method for foreseeing fracture of brittle materials.

Aiming at the self-diagnosis of the fracture in the high-temperature structural materials or refractories, the authors have been trying to detect the applied strain or stress as a function of the change in the electrical properties.¹⁻³⁾ In our previous study, we found out that the electrical conductivity of the $x\text{NiO}-(1-x)\text{CaO}$ ceramics changes by applying the compressive stress,¹⁾ but the working mechanism is not fully understood yet.

In the present study, we evaluate the effect of the compressive stress on the electric conduction of the system $x\text{NiO}-(1-x)\text{CaO}$. In the system NiO-CaO, the volume of the cation site ($\text{Ca}_{\text{Ca}}^{\times}$) is too large for the dissolved Ni^{2+} , whose ionic radius is 0.69 \AA (that of Ca^{2+} is 0.99 \AA).⁴⁾ The large difference in the ionic radii of nickel and calcium is a cause for local deformation of the rock-salt lattice.⁵⁾ Moreover, the weak ligand-field of $\text{Ni}_{\text{Ca}}^{\times}$ and shallow interatomic potential valley of $\text{Ni}_{\text{Ca}}^{\times}-\text{O}_{\text{O}}^{\times}$ are suggested, for the value $10Dq$ (magnitude of the splitting of the d

orbitals by crystal field) of octahedrally coordinated Ni^{2+} in CaO is evaluated by Igarashi *et al.*⁶⁾ and the value is far smaller than that of Ni^{2+} in MgO. Owing to the weak ligand-field of Ni^{2+} in CaO, the bond length of $\text{Ni}_{\text{Ca}}^{\times}-\text{O}_{\text{O}}^{\times}$ is lengthened compared with that of $\text{Ni}_{\text{Ni}}^{\times}-\text{O}_{\text{O}}^{\times}$ in NiO.

Judging from above discussions, dissolved Ni^{2+} in CaO is thought to be quasi stable. If the stress or strain is applied to the NiO-CaO solid solution, it will cause the increase of the internal energy. Considering the instability of the dissolved Ni^{2+} in CaO, we make a hypothesis that the enhanced internal energy would induce the change in the coordination configuration of the dissolved Ni^{2+} in CaO, and that it would affect the electric conduction process of the grains. We guess the origin of the change in the electrical conductivity due to the strain introduced by the applied compressive stress, and discuss the validity of our hypothesis.

II. Experimental Procedure

Calcium carbonate (99.99% in purity, Kojundo Chemical Co., Ltd.) and nickel carbonate (99.9% in purity, Rare Metallic Co., Ltd.) were used as starting materials. They were mixed in a desired proportion with ethanol and calcined in an alumina crucible at 1000°C for 2 hrs. The calcined powder of CaO and NiO mixtures was sieved, and it is uniaxially pressed into rectangular bars with a dimension of $5 \times 3 \times 15 \text{ mm}^3$ under 4.5 MPa. Pressed

powder compacts were sintered at 1400°C for 3 hrs in a platinum boat in air with different temperature profile during cooling processes. For making a quenched specimen, a pressed powder specimen was suspended in the hot zone of the furnace and then dropped out. Except for the quenched specimens, the fired powder compacts were slowly cooled to room temperature at the rate of 200°C/h.

Platinum paste (Tokuriki Chemical Co. Ltd., No.8105) was painted on the both ends of the specimen and platinum electrodes were formed by firing at 1000°C. D.c. two-probe method was used for measuring the electrical conductivity. Fig. 1 shows the experimental setup for the measurement of the electrical conductivity while being loaded. The specimen was sandwiched between alumina plates and set in the center of the furnace of high-temperature mechanical testing system (SHIMADZU Co. Ltd., Model AGS-5kNG). The compressive stress was applied to the specimen at the rate of 20N/min. The measuring temperature was fixed at 1000°C. The deflection and the electrical conductivity of the specimen were simultaneously monitored during the loading.

For determining the lattice parameter, X-ray diffraction (XRD) measurement was conducted on the powdered specimen using CuK α radiation with monochromator.

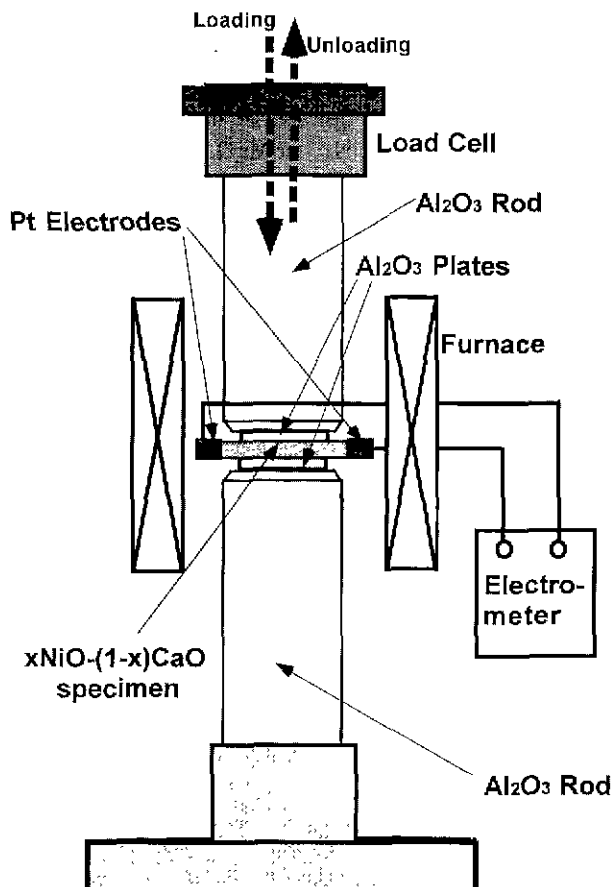


Fig. 1. Experimental setup for the measurement of the strain-dependent electric conduction of ceramics. The measuring temperature is 1000°C.

High purity tungsten was used as an internal standard and the lattice parameter was calculated by Cohen's method. The optical absorption spectrum was measured by using a visible range double-beam spectrophotometer (SHIMADZU Co. Ltd., Model UV-3101PC). For the measurement of the reflection spectrum, the integrated focusing unit (SHIMADZU Co. Ltd., Model ISR-260) was attached to the spectrometer and Al₂O₃ powder was used as a reference.

III. Results and Discussion

The obtained specimens ($x\text{NiO}-(1-x)\text{CaO}$; $x=0.001-0.05$) are pink and their optical absorption peaks are located at 490 nm. The absorption spectra are in good agreement with those reported by Igarashi *et al.*⁶⁾ NiO and CaO are in rock-salt structure, but the system NiO-CaO does not make complete solid solution but belongs to the eutectic system. According to the phase diagram by Smith,⁷⁾ the solid solubility limit of NiO in CaO is about 4% at 1400°C, while that at 1000°C is speculated to be 1% or less. When the $x\text{NiO}-(1-x)\text{CaO}$ specimens with NiO in excess of solid solubility limit ($x > 0.02$ at 1000°C) are annealed at 1000°C, their color changes from pink to gray. The change in color would mean the change in coordination structure of Ni(II)O₆ clusters. Being kept at 1000°C, part of the dissolved NiO is excluded and segregated on the surface or along the grain boundaries and that would be also the origin of the change in color. The color of the $x\text{NiO}-(1-x)\text{CaO}$ specimen which contains NiO less than the solid solubility limit ($x < 0.01$ at 1000°C) turns to pink tinged white by annealing at 1000°C.

1. Strain dependence of the electrical conductivity

As shown in our previous study, when the compressive stress is applied to the $x\text{NiO}-(1-x)\text{CaO}$ specimen, its

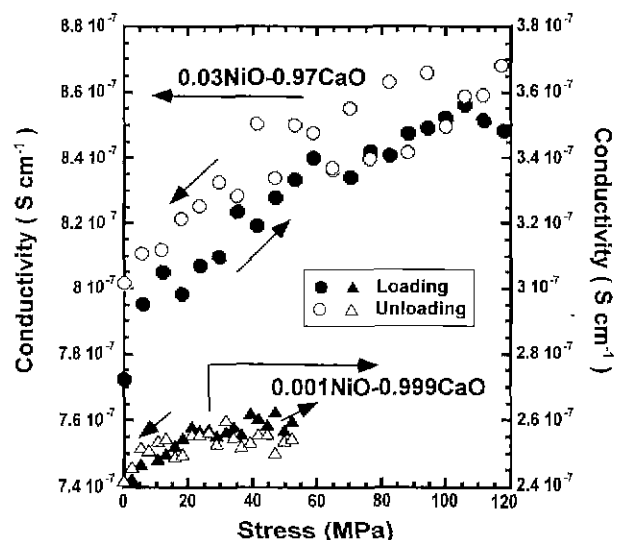


Fig. 2. The stress-conductivity curves of the $x\text{NiO}-(1-x)\text{CaO}$ ($x=0.001$ and 0.03) measured at 1000°C.

electrical conductivity increases with the applied stress.¹¹ The stress-conductivity curves of the $x\text{NiO}-(1-x)\text{CaO}$ with $x=0.001$ (within the solid solubility limit at 1000°C) and $x=0.03$ (over the solid solubility limit at 1000°C) are shown in Fig. 2. The magnitude of the change in the electrical conductivity is extremely small when the NiO content of the specimen is less than the solid solubility limit at the measuring temperature. However, in the specimen which contains NiO over the solid solubility limit, prominent strain dependence of electrical conductivity is observed. The relation between the NiO content (x) and the magnitude of the change in the electrical conductivity by the applied load (47 MPa) is shown in Fig. 3. In the region of $x > 0.01$ (over the solid solubility limit at 1000°C), the magnitude of the change in the electrical conductivity is appeared to be independent of the NiO content.

The stress-conductivity relation of the $x\text{NiO}-(1-x)\text{CaO}$ specimen shows hysteresis and it becomes larger and larger with an increase in loading-unloading cycles. As the loci of the stress-strain curve are unchanged by cyclic loading test at 1000°C , our specimens are apparently elastic in compression in the range of 0-60 MPa loading. It is suggested that the deformation of the specimen by compressive loading is elastic, but the change in the electrical conductivity is not perfectly reversible in the cyclic loading test. Fig. 4 shows the SEM photograph of the $0.01\text{NiO}-0.99\text{CaO}$ (A) before and (B) after loading test. A slight change in the microstructure is observed between the SEM micrographs of (A) and (B). As Fig. 4(A) shows, cubic crystallites, which are typical for the rock-salt type crystal are observed in each grain before loading test. Once the compressive stress is applied to

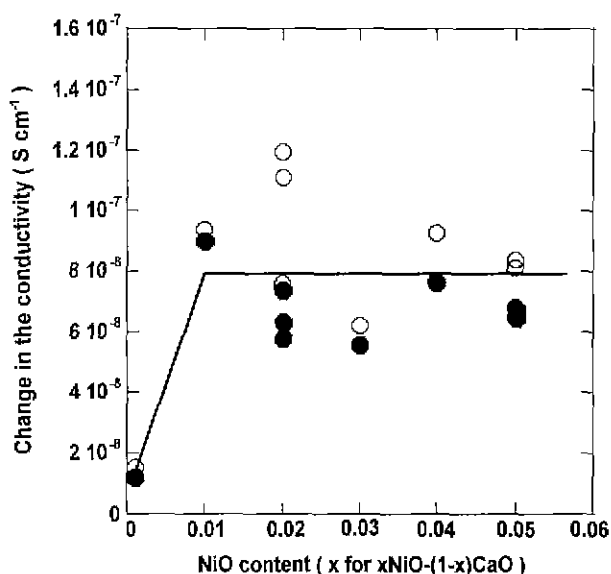


Fig. 3. The relation between the NiO content x for $x\text{NiO}-(1-x)\text{CaO}$ and the change in the conductivity by the applied stress of 47 MPa. Closed circles of the figure are the data under loading and open circles are those under unloading.



(A) 0.01NiO-0.99CaO :
As-prepared



(B) 0.01NiO-0.99CaO :
After loading test

Fig. 4. The SEM micrographs of $0.01\text{NiO}-0.99\text{CaO}$ (A) as-prepared and (B) after the cyclic loading test at 1000°C .

the specimen, the cubic crystallites disappear and local densification takes place, as shown in Fig. 4(B). Such a change in the microstructure would be the origin of the hysteresis of the strain-conductivity curves shown in Fig. 2, but details are not well understood.

2. Lattice parameter elongation by applied compressive stress

Along with the change in the microstructure, the lattice parameter of the $x\text{NiO}-(1-x)\text{CaO}$ specimen changes by applying the compressive stress. The composition dependence of the lattice parameter of the $x\text{NiO}-(1-x)\text{CaO}$ with and without applied load at 1000°C is shown in Fig. 5. It was found that the lattice parameter becomes lengthened by applying compressive stress in all of the compositions, and the magnitude of the increase in the lattice parameter is independent of the NiO content (x) in the region of $x >$

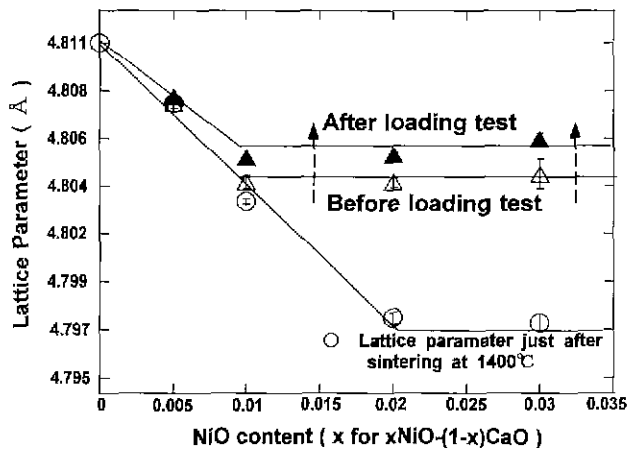


Fig. 5. The lattice parameter of the $x\text{NiO}-(1-x)\text{CaO}$ for $x=0.001-0.03$ before (Δ) and after (\blacktriangle) the cyclic loading tests at 1000°C .

0.01 (over the solid solubility limit at 1000°C).

As for the origin of the elongation of the lattice parameter by applied load, (1) change in the coordination configuration of $\text{Ni}(\text{II})\text{O}_6$ clusters in CaO , or (2) exclusion of NiO from CaO matrix, would be considered. For the discussion on the origin of the strain dependent electric conduction of the $x\text{NiO}-(1-x)\text{CaO}$, it is essential for considering the effect of lattice parameter elongation on the electric conduction process of the $x\text{NiO}-(1-x)\text{CaO}$. This effect will be discussed hereinafter.

3. The effect of lattice parameter elongation on the electric conduction

We have also tried to change or control the lattice parameter of the $x\text{NiO}-(1-x)\text{CaO}$ without applying the stress or strain. The lattice parameter of the $x\text{NiO}-(1-x)\text{CaO}$ can be changed by changing the heating-cooling process of the specimen, i.e. there is large difference in the lattice parameter between the specimens made by quenching and by slow cooling during the fabrication process. The lattice parameter of the $0.03\text{NiO}-0.97\text{CaO}$ specimen made by firing at 1400°C and quenching is far larger than by slow cooling. Calculated lattice parameters of both specimens are summarized in Table 1.

We had already reported the variation in the absorption spectra of the $x\text{NiO}-(1-x)\text{CaO}$ with the sintering tem-

Table 1. The Lattice Parameter of the $0.03\text{NiO}-0.97\text{CaO}$ Fabricated by (A) Firing at 1400°C then Quenching and (B) Firing at 1400°C then Slow Cooling at the Rate of $-200^\circ\text{C}/\text{h}$

Specimen	Lattice parameter (Å)
(A) $0.03\text{NiO}-0.97\text{CaO}$ quenched from 1400°C	4.79937 ± 0.00066
(B) $0.03\text{NiO}-0.97\text{CaO}$ slow cooled from 1400°C	4.79729 ± 0.00043
(C) CaO	4.811

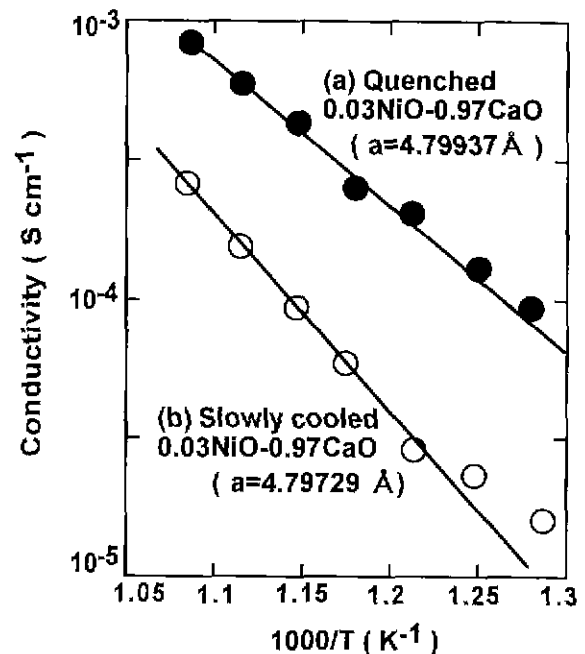


Fig. 6. Temperature dependence of the electrical conductivity of the $0.03\text{NiO}-0.97\text{CaO}$ specimens fabricated by (a) quenching from the sintering temperature (1400°C) (\bullet) and (b) slow cooling from 1400°C at the rate of $200^\circ\text{C}/\text{h}$ (\circ).

peratures.⁶⁾ Production of the expanded $\text{Ni}-\text{O}$ bond in $\text{Ni}(\text{II})\text{O}_6$ cluster in CaO matrix is suggested by the absorption spectra with the peak of 490 nm (which is the origin of the "pink" body). Enhanced 490 nm peak is observed in the specimen sintered over 1200°C . The change in the absorption spectra by high temperature sintering would be correlated with the elongation of the apparent ionic radii of the Ni^{2+} in CaO matrix. The value $10Dq$ of octahedrally coordinated Ni^{2+} in CaO single crystals ($\text{Ni}_{\text{Ca}}^{2+}$) is known to be far smaller than that of Ni^{2+} in MgO or NiO ⁶⁾ and such a weak ligand-field of $\text{Ni}_{\text{Ca}}^{2+}$ would be the origin of the shallow interatomic potential valley of $\text{Ni}_{\text{Ca}}^{2+}-\text{O}_6^{2-}$ and/or of the expanded bond length of $\text{Ni}_{\text{Ca}}^{2+}-\text{O}_6^{2-}$. It is suggested that the expanded lattice parameter of the high temperature sintered $x\text{NiO}-(1-x)\text{CaO}$ would be due to the expanded $\text{Ni}-\text{O}$ bond produced by high temperature firing. The shortening of the lattice parameter of the $0.03\text{NiO}-0.97\text{CaO}$ by slow cooling during the fabrication process would be due to the variation in the coordination configuration of the $\text{Ni}(\text{II})\text{O}_6$ clusters from the expanded type (origin of the pink color) to the normal type (origin of the green color) by lower temperature annealing during the cooling process.

Fig. 6 shows the electrical conductivity of the $0.03\text{NiO}-0.97\text{CaO}$ specimen which was (a) quenched and (b) slowly cooled after sintering at 1400°C . Judging from above discussions, all of the octahedral $\text{Ni}(\text{II})\text{O}_6$ clusters in the specimen (a) have expanded $\text{Ni}_{\text{Ca}}^{2+}-\text{O}_6^{2-}$ bonds. It is suggested that part of the expanded $\text{Ni}_{\text{Ca}}^{2+}-\text{O}_6^{2-}$ bonds turns to the normal octahedral $\text{Ni}(\text{II})\text{O}_6$ clusters during the slow

cooling process. As Fig. 6 shows, the electrical conductivity increases more in case there are higher amount of the expanded octahedral Ni(II)O₆ clusters in the xNiO-(1-x)CaO.

4. The origin of the strain dependent electrical conductivity

If the amount of the expanded octahedral Ni(II)O₆ would increase by applying the compressive stress, we could explain the origin of the increase in the electrical conductivity of the xNiO-(1-x)CaO by applying the compressive stress as the change in the coordination configuration of the Ni(II)O₆ clusters in CaO from the "normal type" to the "expanded type". The result of Fig. 5 suggests the increase in the expanded type Ni(II)O₆ clusters by applying the compressive stress. This hypothesis can also explain the fact that the magnitude of the increase in the lattice parameter is independent of the NiO content x in the region of $x > 0.01$ (Fig. 5), for the NiO content of the grains of each specimen is equal to the limit of solid solution at 1000°C (=1%). At the region of $x > 0.01$ of xNiO-(1-x)CaO, the increase in the electrical conductivity by the 47 MPa applied stress is independent of x (Fig. 3) and the increase in the lattice parameter by the cyclic load test is also independent of x at $x > 0.01$ (Fig. 5). Comparing the data of Figs. 3 and 5, the increase in the electrical conductivity by the stress application is suggested to be due to the increase in the electrical conductivity of the grains of each specimen, whose composition is fixed as 0.01NiO-0.99CaO for all the specimen of the xNiO-(1-x)CaO ($x > 0.01$). A little change in color, from gray to dark brown, is observed between before and after the loading test in the 0.03NiO-0.97CaO. Change in color would be also an evidence for the change in the coordination structure of the Ni(II)O₆ clusters by applying the compressive stress.

If we regarded the origin of the expanded lattice parameter by the applied stress as the exclusion of NiO from CaO matrix, different hypothesis would have to be considered. In our previous report, we pointed out the possibility that the amount of the excluded NiO would be regulated by the applied stress and the excluded NiO would enhance the grain boundary conductivity. If we suppose that the change in the lattice parameter is due to the exclusion of NiO, the amount of the excluded NiO phase is obtained as a function of NiO content by applying the Vegard's law. However, judging from the data of the elongation of the lattice parameter shown in Fig. 5, 10~30% of the dissolved NiO is expected to be excluded from CaO matrix, however, the amount of the "excluded" NiO is too small to make a conduction pass by the excluded NiO layer on the grain boundaries. Moreover, the rapid response to the applied stress is against this hypothesis. When the applied stress is removed, the enhanced electrical conductivity turns to be initial value in a few seconds. The recovering process should be re-dissolution

of the excluded NiO to the CaO grains, but it is unlikely that such a re-dissolution process of the excluded NiO proceeds so rapidly. The previous working model of the strain dependent electric conduction, which is based on the "applied stress induced exclusion-dissolution process of NiO from/to CaO" is judged to be improbable.

Guessing from above discussions, the origin of the strain dependent electric conduction observed in the xNiO-(1-x)CaO specimen would be due to the change in the electrical conductivity of the grains of the specimen, which is introduced by the change in the coordination configuration of the Ni(II)O₆ clusters from normal type (green) to expanded type (pink). Fig. 6 shows that the quenched xNiO-(1-x)CaO specimen shows higher electrical conductivity than the slowly cooled one. The quenched specimen contained high amount of the expanded type Ni(II)O₆ clusters. The enhanced electrical conductivity of the quenched xNiO-(1-x)CaO specimen would be due to the enhanced hopping conduction between the expanded type Ni(II)O₆ clusters. If the part of the normal Ni(II)O₆ clusters in the grains of the xNiO-(1-x)CaO specimen changed to expanded type by applying the compressive stress, the electrical conductivity of the specimen will be enhanced. Due to the weak ligand-field of Ni_{Ca}^x and shallow interatomic potential valley of Ni_{Ca}^x-O_O^x, the expanded type Ni(II)O₆ clusters in the high-temperature sintered specimens would be quasi-stable. In the xNiO-(1-x)CaO at 1000°C, the majority of the dissolved Ni²⁺ in CaO would exist as the expanded type Ni(II)O₆ clusters but part of them turns to the normal type Ni(II)O₆ clusters. When the internal energy is increased by applying the stress, the vibration state of the normal Ni(II)O₆ clusters in CaO would be excited and they turn to quasi-stable state, "expanded type Ni(II)O₆ clusters". As a result, the electric conductivity of the grains of the xNiO-(1-x)CaO specimen will be enhanced. The theoretical analysis of the higher electrical conductivity of the xNiO-(1-x)CaO with "expanded type Ni(II)O₆ clusters" had not been conducted, but the result in Fig. 6 gives an experimental evidence of the higher conductivity of the specimen containing the "expanded type Ni(II)O₆ clusters".

IV. Conclusion

The effect of the applied stress on the electrical conductivity of the NiO-CaO ceramics is investigated and the correlation between the electrical conductivity and the coordination configuration of Ni(II)O₆ clusters in CaO is mainly discussed. Nickel (Ni²⁺) ions in CaO show two types of coordination configuration, those are "normal type" and "expanded type". High temperature sintered NiO-CaO specimen contains high amount of the expanded type Ni(II)O₆ clusters which are stable over 1200°C. The electrical conductivity of the NiO-CaO specimen with expanded type Ni(II)O₆ clusters is guessed to be higher than that of the specimen containing the normal type

clusters. Before the cyclic loading test, the specimen is annealed at 1000°C and part of the expanded type Ni(II)O₆ clusters in CaO would turn to the normal type ones. When the compressive stress is applied to the specimen, the normal type Ni(II)O₆ clusters return to the expanded type again due to the increase in the internal energy and that would be the origin of the strain sensitive electric conduction phenomena shown in Fig. 2.

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