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Electrical properties and microstructure of CuO ceramics containing small amounts of alkaline earth elements

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Abstract

In order to develop suitable materials for ceramic resistors as a final target, basic investigation about electrical properties and microstructure of CuO ceramics doped with some amounts of alkaline earth oxide was performed. The resistivity of CuO ceramics containing additives (MgO, SrO, BaO) with a certain concentration range were lower and showed peculiarly better near linearity in a high applied field of 500 kV/m compared with that of non-doping CuO ceramics. Results of microstructure and crystalline phase analyses of these samples indicated that the additive small grains, whose size was sub-micrometer order, were present dispersively into the CuO grains. Such the change of microstructure of CuO ceramics was thought to induce the peculiar electric properties.
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Keywords: Composite; CuO; Electrical conductivity; Microstructure-final; Transition metal oxides

1. Introduction

Copper oxide (CuO) is well known as a key component materials of many types of high T_c (transition temperature) superconducting ceramics, for example, $Ba_2YCu_3O_{9-\delta}$ and $Bi_2Sr_2CuO_{6+\delta}$, and so on.[1,2] From experimental and theoretical results performed by many researchers, CuO ceramics are imagined to be electrically interesting materials, however, the research about CuO ceramics itself is little and as a result, the knowledge of electric properties and crystalline analyses are not clarified yet. Recently, the authors have found out that alkaline or alkaline earth oxides act as the sintering aid of CuO ceramics and the CuO samples including small amounts of those additives show good linearity of their resistivity at high applied field.[3] If such electrically peculiar characteristics of the CuO-based ceramics could be used, a new type or high performance ceramic resistor will be developed for the component equipments in fields of generation and delivery power systems, for example, transformers, circuit breakers, arrestors.[4] Therefore, it is important to obtain the basic knowledge about CuO and CuO ceramics including additives. Based on the earlier background, the electric properties and microstructure analyses of the CuO-based ceramics are investigated in this paper.

2. Experimental

2.1. Sample preparation

CuO-based ceramics were synthesized as follows. CuO powder (3N, Kojundo Chemical Lab, Co. Ltd.,) and additives powder such as MgO, $SrCO_3$ and $BaCO_3$ (3N, Rare metallic, Co. Ltd., for MgO, and 3N, Kojundo Chemical Lab, Co. Ltd., for other carbonates reagents) were mixed by a wet ball milling method with a distilled water for 20 h, and formed into disk shapes of 1.5×10^{-2} m diameter and 0.3×10^{-2} m thickness by uniaxial pressing. The additive amounts to the CuO powders were from 1.0 to 50.0 mol%, respectively. The obtained green bodies were then sintered in air at 1223 K for 1 h. Non-doping CuO ceramics were also obtained through the earlier procedures. For measuring the electrical properties, both surfaces of the sintered bodies were ground and then silver paste electrodes were formed on both surfaces.

2.2. Sample characterization

In order to evaluate the ohmic characteristics, voltage–current (V–I) characteristics of the samples were

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measured in an electric field of up to 500 kV/m using an ordinary electric tester for low voltage region and an impulse voltage generator (ASG-1kA, Pulse Electronic Engineering, Co. Ltd.,) for high applied field in order to avoid heating of the samples. The resistivity was calculated using the resistance, area of electrode and thickness of the sample.

In order to know the mechanical toughness of samples against electric energy, the energy withstanding capability of samples was evaluated by applying half-wave of alternative voltage (frequency: 50 Hz) from a generator (Pulse Electronic Engineering, Co. Ltd.,) to the sample. The value of energy withstanding capability (EWC) was calculated by the following formula:

$$\mathrm{EWC}\ \left(\mathrm{MJ/m^3}\right) = \left(V_{\mathrm{peak}}/\sqrt{2}\times I_{\mathrm{peak}}/\sqrt{2}\times t\right)/V, \qquad (1)$$

where $V_{\mathrm{peak}}/\sqrt{2}$ and $I_{\mathrm{peak}}/\sqrt{2}$ are the effective value of voltage and current, respectively, t the duration time (10×10^{-3} s) and V the volume of sample.

Crystal phases and microstructure of the samples were analyzed by the X-ray diffraction method (XRD, RU-200, Rigaku International Corporation), scanning electron microscopy (SEM, S-4300, Hitachi Ltd.,) and transmission electron microscopy (TEM, H-800, Hitachi Ltd.), respectively.

3. Results and discussion

3.1. Electrical properties

3.1.1. Behavior of resistivity

All samples synthesized in this study showed good ohmic behavior in V–I characteristics within low applied field. Fig. 1 shows the typical experimental result of the resistivity of the CuO samples against the applied field. As shown in Fig. 1, the resistivity of non-doping CuO ceramics decrease gradually with increasing the applied voltage, that is, it is hard to maintain the initial resistivity (ca. 5 Ωm) in the range of high field. On the other hand, all of the CuO samples containing small amounts of alkaline earth element show good near linear resistance properties to an ultra high-applied field of 500 kV/m, that is, the resistivity seems to be insensitive to the intensity of the electric field. Such excellent ohmic behavior in the high field is seldom observed in other oxides (ZnO, Fe_2O_3, etc.). In the case of non-doping CuO sample, reproductivity of the resistivity and its linearity at the high applied field was not good, hence, non-doping CuO ceramics are thought to be unstable electrically. Since the ceramic resistors used in an electric equipment of power system were exposed for ultra high intensity of electric energy, the CuO ceramics containing small amounts of alkaline earth element are considered to have an advantage as resistors.

Fig. 2 shows the change of initial resistivity of CuO ceramics against the amount of additives [(A) MgO, (B) $SrCO_3$]. As shown in Fig. 2, adding small amounts of MgO or SrO up to ca. 5 mol% gives very low resistivity to CuO ceramics, for example, that of the sample containing 3 mol% SrO (5 mass% $SrCO_3$) is about 0.1 Ωm resulting in good conductivity. The initial resistivity of the samples having such a small concentration range is certified to be stable. In the case of over 5 mol% adding to CuO, the resistivity tends to increase, however, the degree of increase of the case including MgO is extremely large ($\geq$ 2 kΩm), which is different from that of SrO. XRD analyses of these two samples will be discussed in Section 3.2.

3.1.2. Energy withstanding capability

Table 1 indicates the result of evaluation of the energy withstanding capability of the CuO samples including 3

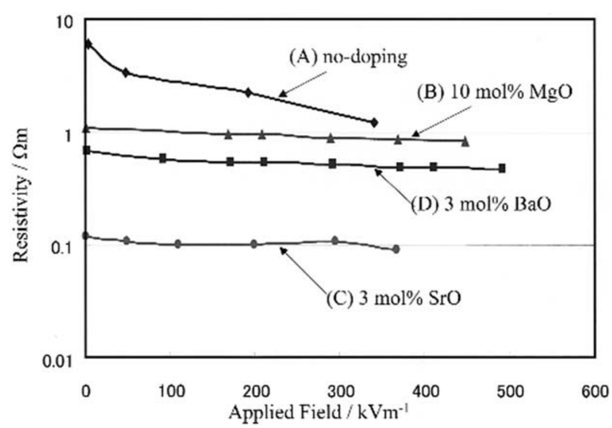

Fig. 1. Typical behaviors of the resistivity of CuO samples against applied field: (A) without additives, (B) with 10 mol% MgO, (C) with 3 mol% SrO and (D) 3 mol% BaO, respectively.

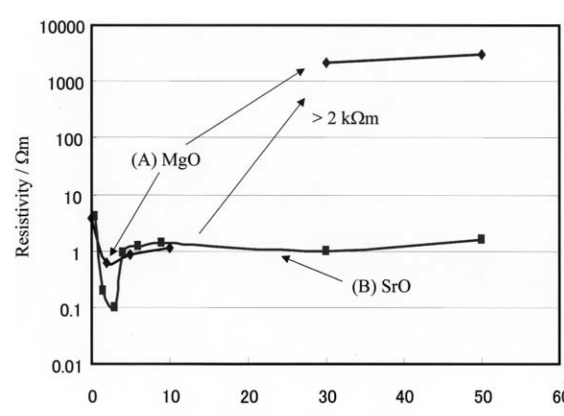

Fig. 2. Change of the initial resistivity of CuO samples containing alkaline earth element against the amount of additives: (A) MgO and (B) SrO.

Table 1
Energy withstanding capability of CuO ceramics including 3 mol% BaO

Voltage/V	Current/A	Energy withstanding capability/MJm^{-3}
290	27.5	170.5
410	39.0	340.7
460	45.5	430.3

mol% BaO. The sample holds out against increasing the applied voltage up to 400 V and the calculated value of energy withstanding capability is over 400 MJ/m^3, which means that this sample has a good potential as ceramic resistors for power systems. However, there are several unknown factors about energy capability of ceramics,[5,6] so a detailed investigation including the reproductivity or the improvement of EWC will be needed.

3.2. Microstructure and crystalline phase analyses

Fig. 3 shows SEM photographs of the fractured surface of CuO samples: (A) non-doping, (B) with 3 mol% SrO, (C) with 4 mol% SrO and (D) with 30 mol% SrO, respectively. It is clear that non-doping CuO has a porous texture. On the other hand, the grain growth in the samples (B) is observed by adding small amount of SrO component. Such a result is also obtained in the case of CaO doping to CuO.[3] In the case of further doping of SrO to CuO (C), the texture is resemble to that of non-doping CuO (A), but the surface of each grain is seemed to be disturbed. Such phenomenon is more remarkable in the case of CuO sample with high concentration doping (D). These disturbed parts onto the grain are estimated to be an Sr component from detailed SEM observation. On the contrary, in the case of MgO doping to CuO, the change seen in Fig. 3 is not apparently recognized.

Fig. 4 shows results of TEM observation in the vicinity of grain boundary (GB) of the CuO samples (A) non-doping and (B) with 3 mol% SrO. As shown in Fig. 4, in the case of non-doping CuO, several dislocations are partly observed as a whole in the CuO grains. Furthermore, the bonding line of GB is relatively sharp and it is thought that there is not any another phase in the vicinity of GB. On the other hand, there are some small grains whose sizes are sub-microns into the main grain or at the GB of the CuO including small amounts of SrO (B). The resemble result is also obtained in the

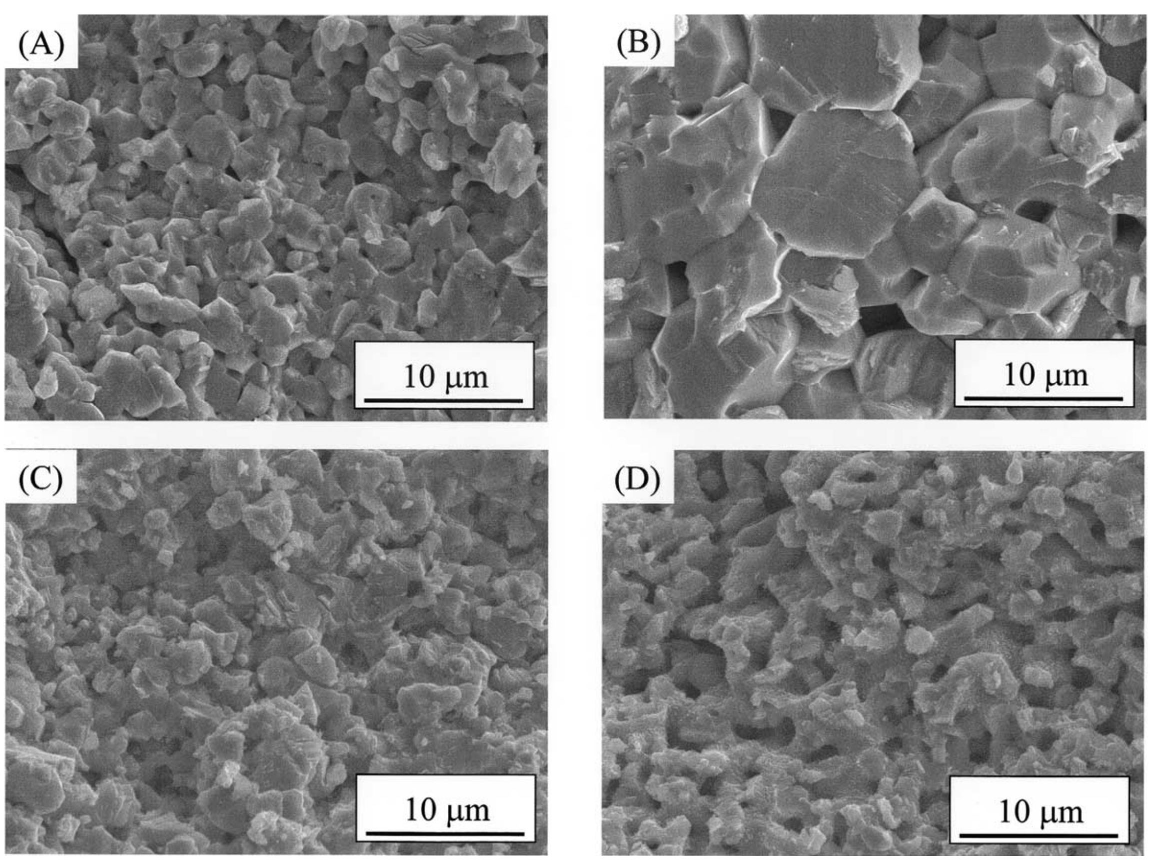

Fig. 3. SEM photographs of the fractured surface of CuO samples: (A) non-doping, (B) with 3mol% SrO, (C) with 4 mol% SrO and (D) with 30 mol% SrO, respectively.

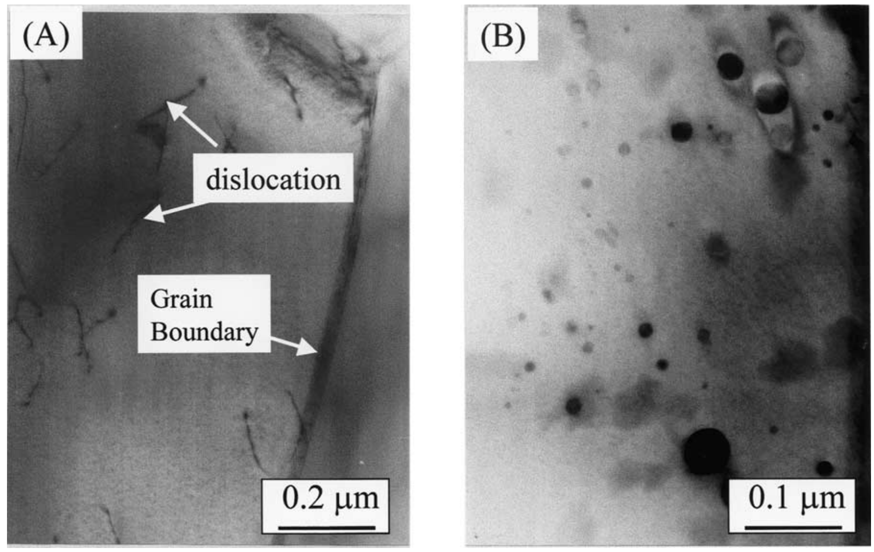

Fig. 4. TEM photographs in the vicinity of grain boundary of the CuO samples (A) non-doping and (B) with 3 mol% SrO.

case of CuO–BaO system. Based on these experimental results, the texture that the small grains due to the additive alkaline earth elements are present dispersively into the CuO grains and/or at the GB are thought to be one of the structural features of CuO ceramics with small amounts of additives.

Fig. 5 illustrates XRD patterns of the CuO samples: (A) with 3 mol% SrO, (B) with 4 mol% SrO, (C) with 10 mol% SrO and (D) with 10 mol% MgO, respectively. As shown in Fig. 5, all XRD peaks in the sample containing <3 mol% (A) are assigned for CuO, however, there appears to be other undefined peaks which might be Sr–Cu–O complex oxide compounds in the sample doped with a little excess SrO (B)–(C). It is found out that further doping of the SrO component, for example, in the case of 30 mol% doping, induces a rapid decrease in intensity of CuO peaks and dominates the earlier mentioned peaks due to the Sr–Cu–O compounds. On the other hand, in the case of doping of MgO, the same results as those of doping of SrO are also obtained except that the peaks are well identified by Cu_2MgO_3.

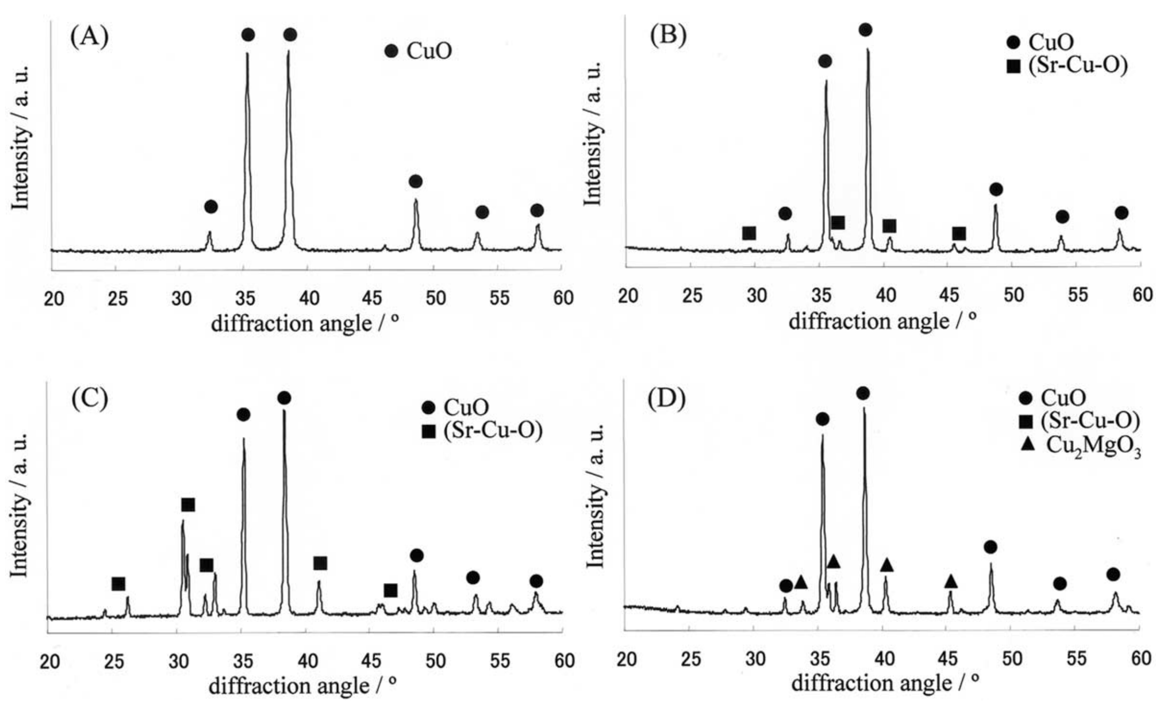

Fig. 5. XRD patterns of the CuO samples: (A) with 3 mol% SrO, (B) with 4 mol% SrO, (C) with 10 mol% SrO and (D) with 10 mol% MgO, respectively.

Based on these analyses mentioned earlier, it is considered that the small doping of alkaline earth element to CuO does not affect the skeleton of matrix CuO presenting dispersively as small grains into the CuO grains. On the contrary, further doping of alkaline earth element induces the compositional inhomogeneity due to the complex compounds. Therefore, the change of structural and/or crystalline phases are connected to appear as peculiar good electric properties of the CuO samples containing small amounts of alkaline earth component. Actually, in the case of the CuO sample, including high concentration MgO or SrO, excellent linearity of the resistivity at the applied high voltage shown in Fig. 1 is not obtained. The detailed analysis of a conductive mechanism and the improvement of other electrical characteristics of this CuO-based ceramic are the subjects of future work.

4. Conclusion

In order to obtain suitable materials for ceramic resistors as a final target, basic investigation about electrical properties and microstructure of CuO ceramics doped with some amount of alkaline earth oxide were performed. The linearity of the resistivity of the CuO including small amounts of alkaline earth additives was better than that of non-doping CuO, which meant they had good potential as ceramic resistors for applying in the field of power system. Microstructure changes that the small grains due to kinds of additives were dispersive in the matrix CuO grains were thought to connect to appear the above excellent electrical properties.

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