PTCR Effect in W-Doped KNbO_3 Ceramics Sintered in Reducing Atmosphere

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還元焼成した W 添加 KNbO_3 セラミックスの PTCR 効果

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Electrical properties of W-doped KNbO_3 ceramics were studied by combining their diffuse reflectance measurements. In the case of samples sintered in a reducing atmosphere, $\text{CH}_4/\text{Ar}=1/99$, they were conductive and two step of positive temperature coefficient of resistivity (PTCR) effects were observed at temperatures where ferroelectric phase transitions from orthorhombic to tetragonal (T_r) and successively to cubic (T_c) occurred, while the resistivities higher than $10^6 \Omega\text{cm}$ were observed for those sintered in air. The 0.2 mol% W-doped sample sintered in the reducing atmosphere showed room-temperature resistivity of 10^1 – $10^2 \Omega\text{cm}$, with PTCR jump ($\log R_{\max}/R_{\min}$) of about 1.4 order of magnitude. Diffuse reflectance measurements for the samples sintered in the reducing atmosphere also indicated an increase of the conduction electron concentration with increasing doped amount of W.

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1. Introduction

KNbO_3 has recently attracted attention for its strong non-linear electro-optical effect.^{1)–3)} It exhibits a sequence of phase transitions from high to low temperatures known as : (a) cubic to tetragonal ($T_c=435^\circ\text{C}$) ; (b) tetragonal to orthorhombic ($T_r=225^\circ\text{C}$) ; (c) orthorhombic to rhombohedral (-10°C). These phase transitions are very similar to that observed in BaTiO_3 . In contrast to many studies on BaTiO_3 ceramics industrially used as PTCR thermistors or capacitors, there are few investigations on electric properties of KNbO_3 ceramics. The reason may lie in its low melting point (about 1056°C) which makes it difficult to be sintered and applied with semiconducting properties compatible with those of BaTiO_3 ceramics. Raevskii et al.⁴⁾ reported two step PTCR effects for the first time in KNbO_3 ceramics with 5–20 mass% K_2O – GeO added as sintering aids and annealed in CO gas. The first step of about 2 orders of magnitude in the region of T_r , where the ferroelectric tetragonal to orthorhombic phase transitions took places ; the second step of about 0.5 order of magnitude was observed around the Curie point T_c . However, the room-temperature (R.T.) resistivity in their samples were higher than $10^6 \Omega\text{cm}$, probably because of relatively large amount of K_2O – GeO glass phases in the grain boundary. Theoretical studies on the interfacial segregation in perovskites by Desu and Payne⁵⁾ suggests that transitions between two ferroelectric phases will change the polarization and dielectric constant, leading to substantial variation in the activation energy of trapped electrons in the grain boundary or barrier height, and the possible appearance of PTCR effect associated with ferroelectric to ferroelectric transformations, e.g., in KNbO_3 . Thus, it is interesting further to investigate the electric properties of well-prepared KNbO_3 ceramics in comparison with BaTiO_3 ceramics. This study concerns with the preparation of PTCR KNbO_3 ceramics having low R.T. resistivities and describes their electrical properties.

2. Experimental

High-purity starting materials, Nb_2O_5 (99.99%), K_2CO_3 (99.9%) and WO_3 (99.9%) were weighed to the nominal compositions $\text{KNb}_{1-x}\text{W}_x\text{O}_3$ ($x=0$ – 0.20 mol%, hereafter

denoted as $x\text{W-KN}$). The dopant WO_3 was dissolved in ammoniac water (NH_4OH) and mixed with the other reagents. Applying sol-gel coating method,⁶⁾ these materials were mixed with 1 mol% of $((\text{C}_2\text{H}_5\text{O})_4\text{Si})$ by wet-milling for 48h. The mixture were dried and calcined at 800°C for 2h in air. The calcined powder were ball-milled with polyvinyl alcohol (PVA) added as a binder. After drying, the powder was pressed into disks of $\phi 20 \times 2$ mm. These pellets were finally sintered in air or in a mixture gas of 1 % CH_4 and 99 % Ar (1 % CH_4 – Ar) at 1040°C for 4h. Surfaces of samples ($x=0, 0.1$ and 0.2 mol%) obtained were carefully polished and applied with In–Ga electrode. The resistivity (R) and relative dielectric constants (ϵ_r) were measured by the two-probe method using a computer-controlled impedance analyzer (YHP, Model 4192 A, Japan). The Cole–Cole plots for the complex impedances measured in the range of 5 Hz to 13 MHz at room temperature (R.T.) were made, and ϵ_r were calculated at 100 kHz based on the parallel circuit mode. The temperature dependencies of R and ϵ_r were also examined by slowly heating the samples to about 600°C in a small electric furnace. Changes in the conduction electron concentration (N_d) with the changes of the sintering atmosphere and of the doped amount of W were investigated by measuring of diffuse reflectance spectra in the 300–1300 nm wavelength region using Al_2O_3 as a reference. The reflectance spectra were transformed to the absorption spectra using the remission function :

$$f(R_e) = (1 - R_e)^2 / 2R_e \quad (1)$$

where R_e is the reflectance and $f(R_e)$ is proportional to the absorption coefficient (k), and A is a coefficient proportional to N_d . It seems worth mentioning that free carriers such as conduction electron shows broad absorption band in the region of visible and infrared region (500–1300 nm), the remission function of which can be expressed as $f(R_e) = A\lambda^n$ ($n=1.5$ – 3.5), where λ is the wavelength of absorption light. Thus the relative variation in N_d can qualitatively be followed.^{7),8)}

3. Results and discussion

Samples could be sintered in air to the relative densities of about 90% of the theoretical value. However, both the $x=0.1$ and 0.2 mol% samples remained almost colorless

with spots of light blue color and partly yellow on the surfaces, indicating that most of doped W probably segregated as WO_3 instead of dissolving into Nb sites to produce conduction electron. The resistivities for all the $x=0, 0.1$ and 0.2 mol% samples at R.T. were higher than $10^6 \Omega\text{cm}$. It was not easy in this system to develop semiconductivity properly by sintering in air as in BaTiO_3 , which is usually sintered in air. Then, compositionally the same samples were sintered in a reducing atmosphere of 1 % CH_4 -Ar. Samples thus obtained had a dark-blue color with relative densities of about 90%. The XRD results showed the presence of a single phase of KNbO_3 in all the cases of $x=0, 0.1$ and 0.2 mol%. There was neither change in the peak pattern nor observable shifts in the peaks positions between the samples sintered in air and in the reducing atmosphere. Figure 1 shows the R.T. complex-plane impedance of $x=0, 0.1$ and 0.2 mol% samples sintered in 1 % CH_4 -Ar gas. The Cole-Cole plots for all samples formed semi-circular shapes, showing that the grain boundary resistivity (R_{gb}) was higher than the grain bulk resistivity (R_b) in each sample, although they were sintered in the reducing gas. There may be acceptor states in the grain boundary region which trapped electrons, forming a highly resistive depletion layer as known in BaTiO_3 .^{9),10)} R and R_b of $x=0$ sample are about $1992 \Omega\text{cm}$ and $20 \Omega\text{cm}$. Semiconductivity observed in the W-free sample sintered in reducing gas may be ascribed to the oxygen vacancy produced in the form of $\text{V}_{\text{O}}^{\cdot\cdot} + 2e'$, releasing conduction electron. With x increasing from 0.1 to 0.2 mol%, R decreased from $1652 \Omega\text{cm}$ to $39 \Omega\text{cm}$, while R_b also decreased from about $26 \Omega\text{cm}$ to about $8 \Omega\text{cm}$. The increase in the conductivity with increasing x should be attributed to the dissolution of W into the Nb site as a donor in the form of: $\text{W}_{\text{Nb}} + e'$, which was assisted by the reducing atmosphere. It should be pointed out that free carriers induced by oxygen carriers may also contribute to the enhancement of conductivity in both W-doped $x=0.1$ and 0.2 mol% samples as observed in the W-free sample.

The temperature dependence of resistivity shows two step of PTCT effect in all the $x=0, 0.1$ and 0.2 mol% samples, as presented in Fig. 2. The first step appeared from around T_r ($\sim 200^\circ\text{C}$), while the second started from around T_c ($\sim 400^\circ\text{C}$). The present results are very similar to that reported by Raevskii et al.,⁴⁾ but the R.T.

resistivities are $10^3 \Omega\text{cm}$, $10^3 \Omega\text{cm}$, and 10^1 – $10^2 \Omega\text{cm}$ for $x=0.1$ and 0.2 mol%, respectively, which are 3 or 4 orders of magnitudes lower than that obtained in their samples.⁴⁾ The PTCT jump, $\text{Log } R_{\text{max}}/R_{\text{min}}$, are about 1.2, 1.0 and 1.4 orders of magnitudes for $x=0, 0.1$ and 0.2 mol% samples, respectively. The origin of PTCT effects observed in the present system may be similar to that observed in BaTiO_3 , which are interpreted by the double-layer potential barrier.^{9),10)} Both the W-doped KNbO_3 samples had two PTCT anomalies around T_r and T_c , at which ϵ_r corresponding reached also the respective maxima, as shown in Fig. 3. This is different from the case of BaTiO_3 in which only one PTCT anomaly is observed around T_c , where phase transition from ferroelectric tetragonal phase to paraelectric cubic phase occurs and ϵ_r reaches a maximum. The phase transition from ferroelectric orthorhombic phase to

Fig. 2. PTCT effects in x W-doped KNbO_3 sintered at 1040°C for 4h in 1 % CH_4 -Ar gas.

Fig. 1. Complex impedance of x W-doped KNbO_3 sintered at 1040°C for 4h in 1 % CH_4 -Ar gas.

Fig. 3. $\text{Log } \epsilon_r$ against T of x W-doped KNbO_3 sintered at 1040°C for 4h in 1 % CH_4 -Ar gas.

Fig. 4. Reflectance spectra of 0.1 mol% W-doped KNbO_3 sintered at 1040°C for 4h in air and in 1 % CH_4 -Ar gas, respectively.

Fig. 5. Reflectance spectra of $x\text{W}$ -doped KNbO_3 sintered at 1040°C for 4h in 1 % CH_4 -Ar gas.

ferroelectric tetragonal phase at T_r observed in KNbO_3 probably induces larger change in spontaneous polarization (P_s) than that in BaTiO_3 , leading to the increase in potential barrier height ($e\phi$) and the presence of PTCR effect at T_r , while there is no obvious change in the case of the latter system.

The reflectance spectra of samples sintered in air showed much smaller $f(R_e)$ values than those in the reducing atmosphere as was shown in Fig. 4 for the case of $x=0.1$ mol%, which indicate the very low conduction electron concentration in those sintered in air. Continuous absorption band in the region of visible and infrared region (500–1300 nm) were observed which can be ascribed to the absorption of conduction electron, while the sharp jump near 300 nm in the ultraviolet region are absorption edge of the band gap in KNbO_3 . For comparison, the spectrum of $x=0$ and 0.2 mol% samples sintered in 1 % CH_4 -Ar gas was shown in Fig. 5. $f(R_e)$ increased with the increasing W amount and there was no other extra absorption peak attributable to the localized electron centers. These reflectance spectra can be fitted with $f(R_e) = A\lambda^{2.6-2.8}$ (λ : in nm) in the infrared region (800–1300 nm). The results showed that coefficient A for the samples sintered in 1 % CH_4 -Ar gas increased markedly from 1.05×10^{-9} , 4.95×10^{-9} to 7.53×10^{-9} with increasing the W amount from 0, 0.1 to 0.2 mol%, respectively. The changes in A are consistent with that observed in R.T. resistivity as stated above, indicating an increase in N_d with increasing x .

4. Conclusion

Semiconducting W-doped KNbO_3 ceramics with R.T. resistivity of about $10^1 \Omega\text{cm}$ – $10^3 \Omega\text{cm}$ were obtained by applying sol-gel coating process and sintering in reducing atmosphere, $\text{CH}_4/\text{Ar}=1/99$. Two-step PTCR effects were observed around T_r and T_c in the cases of samples sintered in reducing atmosphere. The $x=0.2$ mol% sample sintered in reducing atmosphere showed room-temperature resistivity of 10^1 – $10^2 \Omega\text{cm}$, with a PTCR jump of about 1.4 order of magnitude. The results of diffuse reflectance measurements for the samples sintered in the reducing atmosphere also indicated an increase of the conduction electron concentration with increasing doped amount of W.

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