Electrical Properties of PbTiO₃ Single Crystals Grown from PbO-Cu₂O Flux Method

Satoshi FUJII, Yosohiro SUGIE, Masafumi KOBUNE and Tomihiko YAMAMOTO*

Department of Applied Chemistry, Faculty of Engineering, Himeji Institute of Technology, 2167, Shosha, Himeji-shi 671-22
*Daizo Co., Ltd., 9, Otakasu-cho, Amagasaki-shi 660

The growth of PbTiO₃ single crystals from PbO-Cu₂O flux method and the electrical properties of the grown single crystals were studied. (1) PbTiO₃ crystals grown from a PbO-Cu₂O (7 wt%) were single crystals, and had a maximum dimension of 4.5\times4.5\times1.7 \text{mm}^3. (2) All crystals contained less than 0.01 wt% Cu ion. Therefore, crystals doped with Cu ion may be shown no variation of the lattice constant. (3) Electrical properties of the crystals were affected by Cu ion. The electrical conductivity of crystals was very low (about \(10^{-12} \text{S cm}^{-1}\) at room temperature. At temperature about 300°C, the current-voltage characteristic curve revealed that the crystal doped with Cu ion was characterized by ohmic and non-ohmic conduction. The critical field strength, \(E_H\) value, decreased remarkably with increasing temperature.

Key-words: PbTiO₃, Single crystal, Flux method, PbO-Cu₂O flux, Conductivity, \(I-V\) characteristics

1. Introduction

PbTiO₃ is an eminent ferroelectric with high Curie temperature, high pyroelectric coefficient, low dielectric constants, and high spontaneous polarization. PbTiO₃ single crystals have been made by using KF,1,2) PbO,3,4) and B₂O₃-PbO5) as fluxes so far, but few satisfactory crystals are obtained by above flux method.

We studied the growth of single crystals to obtain PbTiO₃ crystals with low defect concentrations by using PbO as a flux. As shown in the previous papers,6) PbTiO₃ single crystals with comparably flat surface and high electric resistivity can be obtained by doping with a very small amount of Mg, Sr or Li ions. But the dimension of the grown crystals was not satisfactory for the study on growth of PbTiO₃ crystal (\(\leq 3 \text{mm}\)).

In this work, the growth of PbTiO₃ single crystals by using PbO and Cu₂O mixtures as a flux and electrical properties of the grown single crystals were studied.

2. Experimental method

2.1 Growth of single crystals

PbTiO₃ fine powder (99.9% purity, prepared by Yamana Semiconductor Corp.) was used as a starting material. The mixtures of PbO and Cu₂O powders (guaranteed grade, prepared by Nacalai Tesque Inc.) were used as the flux.

The weight ratio of PbO and Cu₂O in the flux \([\text{Cu}_2\text{O}/(\text{PbO+Cu}_2\text{O})]\) was 0 to 0.14. The weight ratio of the material to flux was 0.4. The material was heated in a platinum crucible (50 ml) by using a vertical electric-resistance furnace. The heating was made at a rate of 200°C/h up to 1000°C for 10 h, and then cooled to room temperature at a rate of 20°C/h. The grown crystals were immersed into diluted nitric acid to dissolve the flux and washed with water, then drying at 50°C for 24 h.

2.2 Characterization

The grown crystals were analysed by X-ray diffraction method (XRD) to determine the phase. The lattice constants of the PbTiO₃ crystals were determined from the (002) and (200) reflection lines using a high purity silicon powder (99.9%) as an internal standard. The precision of the measurement is about \(\pm 0.001 \text{nm}\). The imperfection of the grown crystals was evaluated by the back reflection Laue method, using an XRD photographic device. The surface morphology of the PbTiO₃ crystals was observed using a scanning electron microscope (SEM). The composition of the crystals was determined by an atomic absorption analysis. The electrical properties (current-voltage \(I-V\) characteristics and electrical conductivity \(\sigma_{dc}\)) of grown crystals were measured according to the procedures in a previous paper.6) The precision of the measurement is about \(\pm 1\%\).

3. Results and discussion

3.1 Grown of PbTiO₃ single crystals

Table 1 shows the results obtained for the grown PbTiO₃ in flux mixed with Cu₂O of 0 to 14 wt%. The dimension of crystal for run No. 5 was larger than 4 mm. The analysis showed the presence of Cu ion.
less than 0.01 wt% in all crystals, which proved that
Cu ion was little or only slight incorporated in crys-
tals. Therefore, the XRD pattern of the grown crys-
tals was identified only by PbTiO₃ absence such as
CuO. The lattice constants of the PbTiO₃ obtained in
only PbO flux were a₀=0.390 nm and c₀=0.415 nm.
In the PbTiO₃ crystal doped with Cu ion, there were
no variation in the lattice constants. For this reason,
the content of Cu ion in the obtained crystal was by a
very small amounts from chemical analysis, and the
ionic radius the slight difference (Pb²⁺/Cu⁺=1.25
and Ti⁴⁺/Cu²⁺=0.99). If Ti⁴⁺ is substituted by
Cu²⁺, the crystal obtained may be represented by Pb
(Ti₁₋ₓCuₓ)O₃₋ₓ. Figure 1 shows the SEM photo-
graphs of the crystal for run No. 5. This crystal has
comparably flat surface with dark color, but changed
to highly transparent with red-brown color by polish-
ing of crystal surface. From the Laue spots of the
crystal for run No. 5, the crystal was proved to be a
single crystal with very few defect. The crystal for
run No. 5 has a complex domain structure consisting
of 180° and 90°.

3.2 Electrical properties  
3.2.1 I–V characteristics

Figure 2 shows the I–V characteristics curves
measured for crystal for run No. 5. From this figure,
with in the measurement range, the relation between
current and potential at 100°C and 200°C conforms to
Ohm's law. At temperature above 300°C, the I–V
characteristic curves measured are divided into two,
ranges 1 and 2, in which current depends differently
on the applied voltage. The range 1 is on the lower
electric field side in which the current deviates from
Ohm's law. The range 2 is on the higher electric field
side in which the current deviates from Ohm's law.
As seen from Fig. 2, the V_H value (the limiting ap-
plicated voltage in the range 1) was 40 V at 300°C, 15 V
at 400°C and 5 V at 500°C. In the range 2, the crys-
tals were often broken down during measurements.

3.2.2 Electrical conductivity \( \sigma_{dc} \)

The \( \sigma_{dc} \) of crystal for run No. 5 were measured at a
constant electric field, applied voltage of 15 V. The
results are shown in Fig. 3 and Table 2. The \( \sigma_{dc} \) of
crystal doped with Li ion, also are shown in Fig. 3
and Table 2. While the Arrhenius' plot for the crys-
tal for run No. 5 containing 0.01 wt% of Cu ion is not
linear. The temperature dependence of \( \sigma_{dc} \) for the
crystal can be characterized differently in the follow-
ning three temperature range. The first is from room
temperature to 200°C, the second from 200°C to
450°C and the third above 450°C. The \( \sigma_{dc} \) of crystals
for run Nos. 4 and 6 also resulted about similar to
that described above. The curve be well approximat-
ed by linear with different temperature coefficient de-
pending on each range. For the crystals, $\sigma_d$ in the
range from room temperature to about 150°C is very
low ($\approx 10^{-12}$ S·cm$^{-1}$), comparing with that of un-
doped crystals ($\approx 10^{-6}$ S·cm$^{-1}$). It suggests that a
trace of Cu ion in crystals decreases $\sigma_d$. The
gradient of the curve changes remarkably at near
450°C. This temperature is close to the Curie point
($\approx 490°C$). The change might be related to the phase
transition of the crystal. Comparing with the crystal
with Li ion for run No. 5, an electric resistivity of the
crystal seems to be larger than in the low tempera-
ture and 600°C.

From the gradient of the line in the three tempera-
ture ranges in Fig. 3, an apparent activation energy
$U_a$ of the crystal for run No. 5. was calculated, and
that for the crystal doped with Li ion was also given.
The results are shown in Table 2. The $U_a$ value is
related to the mobility of carriers. The mobility of
 carriers in crystal for run No. 5 seems to be almost
the same as that for the crystal doped with Li ion in
the range from 25 to 450°C.

3.2.3 Critical electric field strength $E_H$

In the non-ohmic region of the $I$–$V$ characteristic
curves of the crystal shown in Fig. 2, the critical elec-
tric field strength $E_H$ ($V_H/0.05$ cm; thickness of crys-
tal) was obtained. From the temperature depend-
ence of $E_H$, the effect of doped Cu ion (0.01 wt%) on
the electrical conductivity of PbTiO$_3$ single crys-
tal and the polarization condition of the crystal for
run No. 5 was examined. Figure 4 shows the $E_H$
value plotted against temperature for the crystals
doped with Cu ion and Li ion. The $E_H$ value for the crystal doped with Cu ion was higher than for the crystal doped with Li ion in the
temperature range between 400 and 500°C. This clearly indicates that the doped Cu ion gives some
effect on the conductivity. The lowest value of $E_H$
for the crystal doped with 0.01 wt% Cu ion was about
100 V/cm or so.

As mentioned above, the crystal doped with 0.01
wt% Cu ion seems to have potential to be applied to
pyroelectric infrared detectors. For that, polariza-
tion treatment must be applied to the crystal, and
it should be made under the electric field with the
strength of 30–50 V/cm. This treatment would pre-
vent the crystal from thermal breakdown which can
be caused by large electric current passing through
the crystal.

4. Conclusion

Single crystals of PbTiO$_3$ were grown from PbO–
Cu$_2$O flux and their electrical properties were stud-
ied. The results are summarized as follows:

1. The grown PbTiO$_3$ crystal in the mixed flux
of PbO and Cu$_2$O (7 wt%) was single crystal doped
with Cu ion, and had a maximum dimension of
$4.5 \times 4.5 \times 1.7$ mm$^3$.

2. The content of Cu ion was less than 0.01
wt% for all crystals and the lattice constant of the
crystal doped with Cu ion showed no variation be-
cause of a very small amount of Cu ion.

3. The electrical conductivity of crystal doped
with Cu ion was very low. At temperatures above
300°C, the $I$–$V$ characteristic curve of the crystal
doped with Cu ion was composed of two parts, ohmic
and non-ohmic one. The critical field strength, $E_H$
value, above which electric current increases inten-
sively decreased remarkably with increasing tempera-
ture.

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