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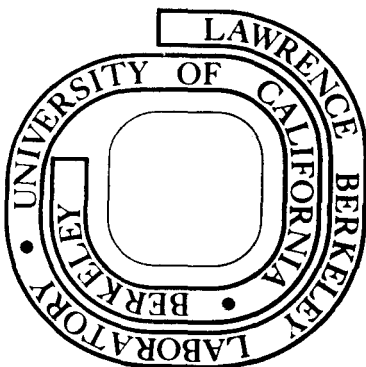
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ELECTRICAL CONDUCTIVITY IN LEAD ZIRCONATE-TITANATE CERAMICS

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ABSTRACT

The electrical conduction in polycrystalline lead zirconate-titanate ceramics was investigated. Polycrystalline compacts of lead zirconate-titanate with various dopants and stoichiometry were fabricated from chemical solutions as well as mixed oxide powder. Sintering using powder technique in 1 atm oxygen was used to control the stoichiometry of the system. DC resistivity was measured by using a guard ring method. Thermoelectric power measurements were also conducted to characterize the type of charge carriers contributing to the conduction process. It is shown that electrical conduction in lead zirconate-titanate follows typical semiconductor behavior. Holes contributed by lead vacancies are the major charge carriers. Impurity ions which can serve as acceptors or donors will significantly affect the conduction process. The activation energy is 3.6 eV for intrinsic conduction and 1.4 eV for extrinsic conduction due to lead vacancies.

INTRODUCTION

Lead zirconate-titanate (PZT) is an important ceramic widely used for piezoelectric devices.[1,2] It is ferroelectric and has a perovskite structure. Electrical conductivity which directly relates to the power loss of the system during use is an important physical parameter. The electrical conduction mechanism in PZT has not been clearly defined. Ikeda et al.[3] gave a brief report on niobia-doped PZT. The resistivity was greatly increased by the addition of Nb_2O_5. Gerson and Jaffe[4] proposed that the electrical conduction in PZT resulted from an excess of lead vacancies. This proposed model has not been verified. Takahashi[5,6] measured the electrical resistivity for lead zirconate-titanate ceramics containing various metal oxides as dopants. It was found that some dopants had no effect, some increased the resistivity, and others increased it first and then decreased it. No complete explanation was given for these results.

A major difficulty which plagued previous investigators in studying the electrical properties of PZT was the control of PbO loss during sintering.[7-9] Recently, Holman and Fulrath[10] established the PbO activity above the $PbTiO_3$-$PbZrO_3$ system. They also determined the single phase width of the solid solutions in the system. Thus, an improved packing powder technique was established that allowed reproducible processing of PZT compositions to a known stoichiometry.[11] In the present work, this fabrication procedure was employed to control the material loss from PZT during sintering. The purpose of this study was to determine the mechanism of electrical conduction in lead zirconate-titanate ceramics. The effects of impurities, temperature, and defect

structures on electrical conduction are discussed.

EXPERIMENTAL PROCEDURE

Sample Preparation

PZT compositions of $Pb(Zr_{0.5}Ti_{0.5})O_3$ containing no dopants, and
2 and 4 mole% $ScO_{1.5}$, and 2 and 4 mole% $NbO_{2.5}$ were prepared from chemi-
cal solutions as well as oxide powders. The raw materials used for chem-
ically prepared PZT were lead oxide powder, zirconium tetra-butoxide
liquid and titanium tetra-butoxide liquid. Scandium oxide and niobium
oxide powder were used as dopant materials. Proper proportions of raw
materials were mixed in a blender and then reacted and co-precipitated
from solution by adding distilled water. The blended slurry was dried
and calcined at 500°C for 24 hours. After calcining, the powder was
milled for 4 hours in isopropyl alcohol using ZrO_2 balls as grinding
media. The powder was calcined again at 500°C for eight hours. After
the second calcination, the powder was again milled for 2 hours. The
powder was then passed through a 325 mesh screen and cold pressed at
10,000 psi in a 1 inch diameter die. The green density of the pressed
pellets was about 2.6gm/cc.

For the purpose of comparison, mixed oxide PZT was prepared from
lead oxide powder, zirconium oxide powder and titanium oxide powder.
Raw materials with dopant oxides were mixed in suitable proportion in a
Sweco ball mill for 4 hours using isopropyl alcohol and ZrO_2 balls as
the grinding media. The alcohol was evaporated and the mixture was cal-
cined at 800°C for 2 hours in a zirconia crucible. After calcining,
5 wt% PbO was added to the powder. The PbO rich powder was milled again,
dried and passed through 80 mesh screen. The powder was cold pressed at
5,000 psi in a 1 inch steel die. No binder was used. The green density

of the pressed pellets achieved 4gm/cc.

Sintering Conditions

All sintering runs began by heating the furnace at a constant rate of 300°C/hr to the sintering temperature, 1200°C. The specimens were held for 16 hours at temperature then cooled at the natural rate of the furnace. The high vapor pressure of PbO necessitated the use of a packing powder to provide an exact known PbO vapor surrounding the pellets. Thus, the sample and the powder were in local atmospheric equilibrium and the material loss from the system could be controlled. Undoped and niobium doped samples were always buried deeply in a packing powder of lead zirconate plus 5 wt% zirconia while sintering in 1 atm oxygen. For scandium doped samples, lead zirconate-titanate plus 5 wt% PbO was used as a packing powder for sintering in 1 atm helium.

Sample Characterization

Density of the sintered samples were measured by water displacement and also by geometric measurements. Theoretical density for PZT was taken as 8gm/cc. For chemically prepared PZT, density of the undoped and niobium doped samples were above 98% theoretical density and that of the scandium doped samples achieved 95%. For mixed oxide PZT, density of the undoped and niobium doped samples were above 99% and that of scandium doped samples were above 90%. X-ray analysis showed the typical PZT phase. No trace of a PbO phase appeared.

For the microstructure examinations, samples were polished and then chemically etched in a 35% HCl solution with three drops of HF per 100 ml of solution. Observations of etched surfaces using scanning electron microscopy are shown in Fig. 1. Both niobium and scandium

served as grain growth inhibitors as observed by Atkin and Fulrath.[12]

Properties Measurement

DC bulk resistivity was measured by using a guard ring method similar to that in Reference 13. Sputtered gold electrodes were used to provide ohmic contacts. The surfaces of all the sintered samples were ground to a depth sufficient to eliminate inhomogeneity due to any surface affects before electrodes were applied. DC voltages provided by dry cells were used for all measurements. Most of the measurements were conducted in the temperature range of 150-500°C. Bidirectional measurements were made and the results from each polarity were averaged to eliminate the thermoelectric contribution to the measured signal.[13]

Thermoelectric power measurements were made to determine the type of charge carrier contributing to the conduction process. The measurement system was calibrated by using p and n type Si wafers.

RESULT AND DISCUSSION

The influence of temperature on the resistivity of the chemically prepared and mixed oxide PZT with various dopants are shown in Fig. 2. The resistivity increases with increasing niobium content and decreases with increasing scandium. There is a straight line relationship between log resistivity and inverse absolute temperature. This is typical for a semiconductor. The resistivity data were usually analyzed according to $\rho = \rho_o \exp(E/kT)$ where ρ is resistivity, ρ_o a constant, E activation energy and k the Boltzman constant. The activation energy for conduction can be calculated from the slope of the straight line segment. Previous investigators[14,15] have already determined that ionic conduction is negligible in the PZT composition used for this study. Measurements of the thermoelectric voltage showed that hole conduction (p-type semiconductor) dominated in all samples.

In considering electrical conduction in ceramic semiconductors, we are mainly concerned with defects and impurities which can serve as donors or acceptors. For undoped PZT, high concentrations of interstitials are unlikely because the perovskite unit cell is already closed-packed and the possible interstitial sites are bounded by both positive and negative ions. Major defects are lead vacancies and oxygen vacancies owing to the high volatility of lead and oxygen in PZT. The p-type conduction suggests that electrical conduction in PZT is due to lead vacancies. An attempt was made to establish sample equilibrium with 1 atm oxygen and different PbO activities. It was found that the resistivity of the sample equilibrated with the high PbO activity is greater than that equilibrated with low PbO activity. This is

consistent with the picture that the electrical conduction in PZT is due to lead vacancies.

It has been established that Nb^{+5} and Sc^{+3} substitute for $(Ti, Zr)^{+4}$ and create lead and oxygen vacancies, respectively, as shown in Fig. 3.[16,17]. The lead vacancy concentration increases with increasing Nb_2O_5 content in the system. However, the experimental results show that the conductivity drops with increasing Nb^{+5} content. This can be explained as a compensation effect.[18] Nb^{+5} can serve as a donor and contribute electrons to the conduction process. According to the law of mass action, this result may lead to the reduction of total charge carrier and thus the resistivity increases with Nb_2O_5 content in PZT.

For scandium doped samples, the concentration of oxygen vacancy increases. The resistivity drops with increasing amount of scandium in PZT. In this case conduction still occurs by the migration of holes (p-type conduction), therefore, electrical conduction can not be totally due to lead vacancies. It is possible that Sc^{+3} ions serve as acceptors. The substitution of Sc^{+3} ions for $(Ti, Zr)^{+4}$ ions creates an acceptor level on the B site in the perovskite structure. The charge carrier concentration also increases with increase in Sc^{+3} content and thus de-creased resistivy is observed.

The activation energy for either intrinsic or extrinsic conduction in a semiconductor can be correlated with the ionization energy. The calculated activation energy was plotted against the amount of dopants as shown in Fig.-4. The activation energy, 1.41 eV, is the same for niobium doped and chemically prepared undoped PZT. This indicates that the conduction mechanism is the same and is due to hole migration

contributed by lead vacancies. The activation energy is low, 1.1 eV, for scandium doped samples. Therefore, Sc^{+3} in solid solution on the B site contributes an acceptor level and gives p-type conduction with a lower activation energy.

Doping, the intentional addition of material for the purpose of modifying properties, can be off-set by the unintentional introduction of impurities during processing. The effect of ball milling impurities on the electrical conductivity of PZT was investigated and the result is shown in Fig. 5. There is a clear difference in the activation energy of the two samples where the difference in specimen preparation was only the milling media used. The activation energy is 1.05 eV for the material ground by an Al_2O_3 grinding media and 1.41 eV for the material ground using ZrO_2 grinding media. Atkin and Fulrath[19] have shown that Al^{+3} ions can go into solid solution in PZT. Because Al^{+3} substitutes for $(Ti, Zr)^{+4}$ on the B site, it has the same effect as Sc^{+3} and leads to a lower activation energy.

The activation energy of the undoped mixed oxide PZT is lower than that of undoped chemically prepared material. This is due to an impurity effect. Zirconium oxide and titanium oxide powders instead of tetra butyl zirconate and the tetra butyl titanate chemical solutions were used as the principal constituents to prepared mixed oxide PZT. Spectrographic analysis showed that the Al_2O_3 content is 0.05% in chemically prepared PZT and 0.3% in mixed oxide PZT.

The exponential dependence of the resistivity on temperature observed by other investigators is shown in Fig.6. The actual resistivity and activation energy from various investigators differ

considerably. These differences are undoubtedly due to impurities present in the samples and the different preparation techniques. There is no information concerning the impurity content of the PZT samples that previous investigators used for their measurements. Gerson and Jaffe's[4] work was performed in the early 1960s. Their samples were sintered in air and no attempt had been made to control the PbO loss. A very low activation energy (0.89 eV) was reported in their study. Takahashi's[5,6] results were published in 1970. He tried to control the PbO loss by surrounding the sample with a packing powder of the same composition during firing. He also had his samples in contact with Pt. Experiments in this laboratory have shown that Pt is a sink for Pb. Therefore, exact PbO activity is unknown and the control of stoichiometry can be questioned. It is interesting to note that the resistivity and the activation energy reported by Takahashi is almost identical to that for a sample ground by an Al_2O_3 grinding media in this study. This clearly shows how important the effect of impurity content in raw materials, impurities introduced during sample processing, and the material loss during firing is on the electrical conductivity.

In studying the electrical resistivity of PZT over the temperature range 150-800°C, a change in activation energy was observed. Above 650°C the activation energy was 3.6 eV. It is suggested that this activation energy is that for intrinsic conduction.

APPENDIX

For an undoped, high purity lead zirconate titanate, ionized lead vacancies as electron acceptors are formed

$$V_{Pb} \rightarrow V_{Pb}{}' + \oplus$$

for the first ionization, and
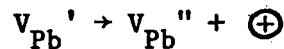
$$V_{Pb}{}' \rightarrow V_{Pb}{}'' + \oplus$$

for the second ionization. Kroeger-Vink notation is used in the equations V_{Pb}, $V_{Pb}{}'$ and $V_{Pb}{}''$ represent a lead vacancy, a singly ionized lead vacancy, and a doubly ionized lead vacancy respectively, and $\oplus$ a conduction hole.

Acceptor levels are produced as a result of addition of Al^{+3} and Sc^{+3}. Holes are generated from the acceptors as

$$Al^{\bullet}_{(Ti,Zr)} \rightarrow Al_{(Ti,Zr)} + \oplus$$
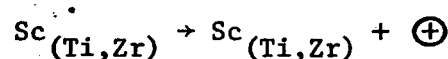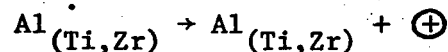
$$Sc^{\bullet}_{(Ti,Zr)} \rightarrow Sc_{(Ti,Zr)} + \oplus$$

where $Al^{\bullet}_{(Ti,Zr)}$ and $Sc^{\bullet}_{)Ti,Zr)}$ are Al^{+3} and Sc^{+3} at a normal (Ti,Zr) site in PZT. $Al_{(Ti,Zr)}$ and $Sc_{(Ti,Zr)}$ are ionized ions.

Substitution Nb^{+5} serves as electron donor. Electrons are generated as
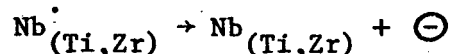
$$Nb^{\bullet}_{(Ti,Zr)} \rightarrow Nb_{(Ti,Zr)} + \ominus$$

where $Nb'_{(Ti,Zr)}$ and $Nb_{(Ti,Zr)}$ represent Nb^{+5} and ionized niobium ions at (Ti,Zr) sites respectively, and $\ominus$ is the conduction election.

ACKNOWLEDGMENT

FIGURE CAPTIONS

Fig. 1. Microstructure of chemically prepared PZT (a) 1 mole% Nb_2O_5 doped (b) 2 mole% Nb_2O_5 doped (c) undoped (d) 1 mole% Sc_2O_3 doped (e) 2 mole% Sc_2O_3 doped.

Fig. 2. Resistivity – temperature characteristics for chemically prepared and mixed oxide PZT.

Fig. 3. Chemical formula for undoped, Sc^{+3} doped and Nb^{+5} doped PZT. □ refers to an ion vacancy.

Fig. 4. Dependence of activation energy for conduction on type and content of dopants in chemically prepared and mixed oxide PZT.

Fig. 5. Effect of ball milling impurities on the electrical resistivity of chemically prepared PZT.

Fig. 6. The temperature dependence of electrical resistivity in polycrystalline PZT as observed by Dih and Fulrath in this work, Gerson and Jaffe[15], and Takahashi.[17]
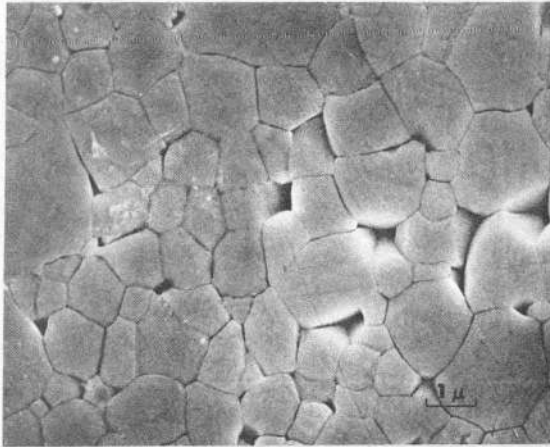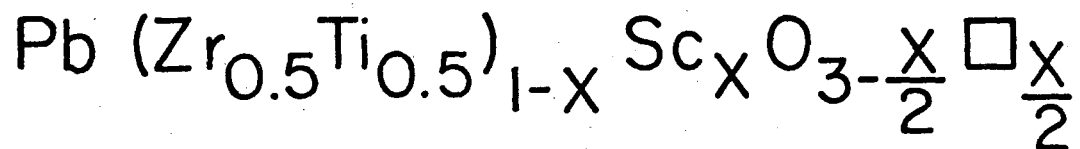
(a)
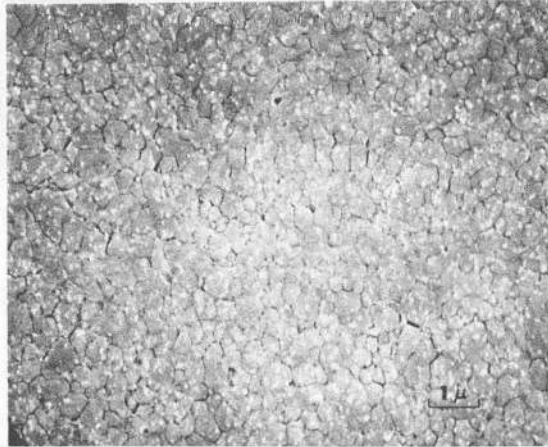
(b)
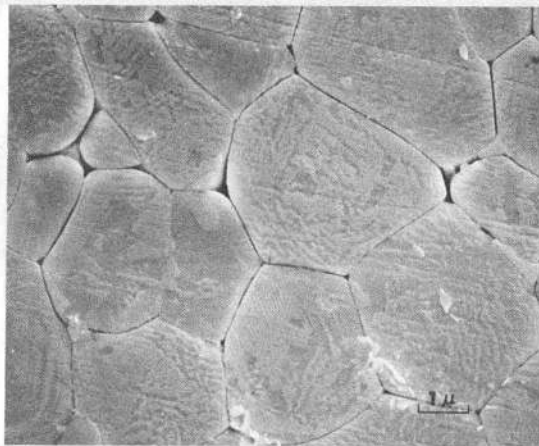
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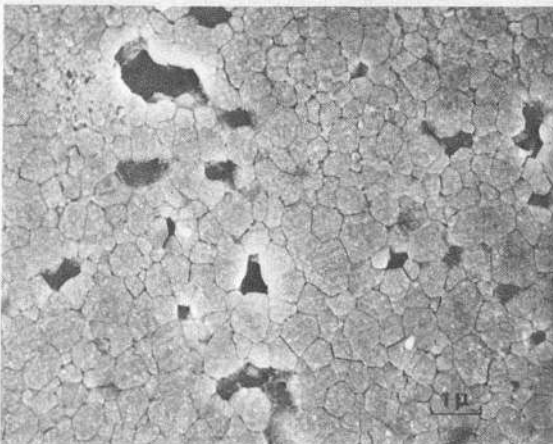
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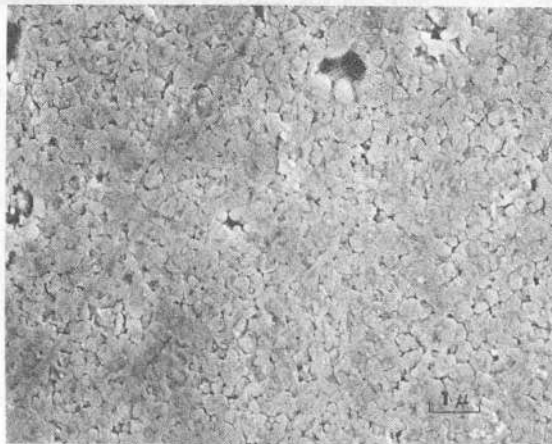
(e)

XBB 762-1931

Fig. 1

XBL 761-6121

Fig. 2

$$Pb\,(Zr_{0.5}\,Ti_{0.5})\,O_3$$

$$Pb_{1-\frac{X}{2}}\,\square_{\frac{X}{2}}\,(Zr_{0.5}\,Ti_{0.5})_{1-X}\,Nb_X\,O_3$$
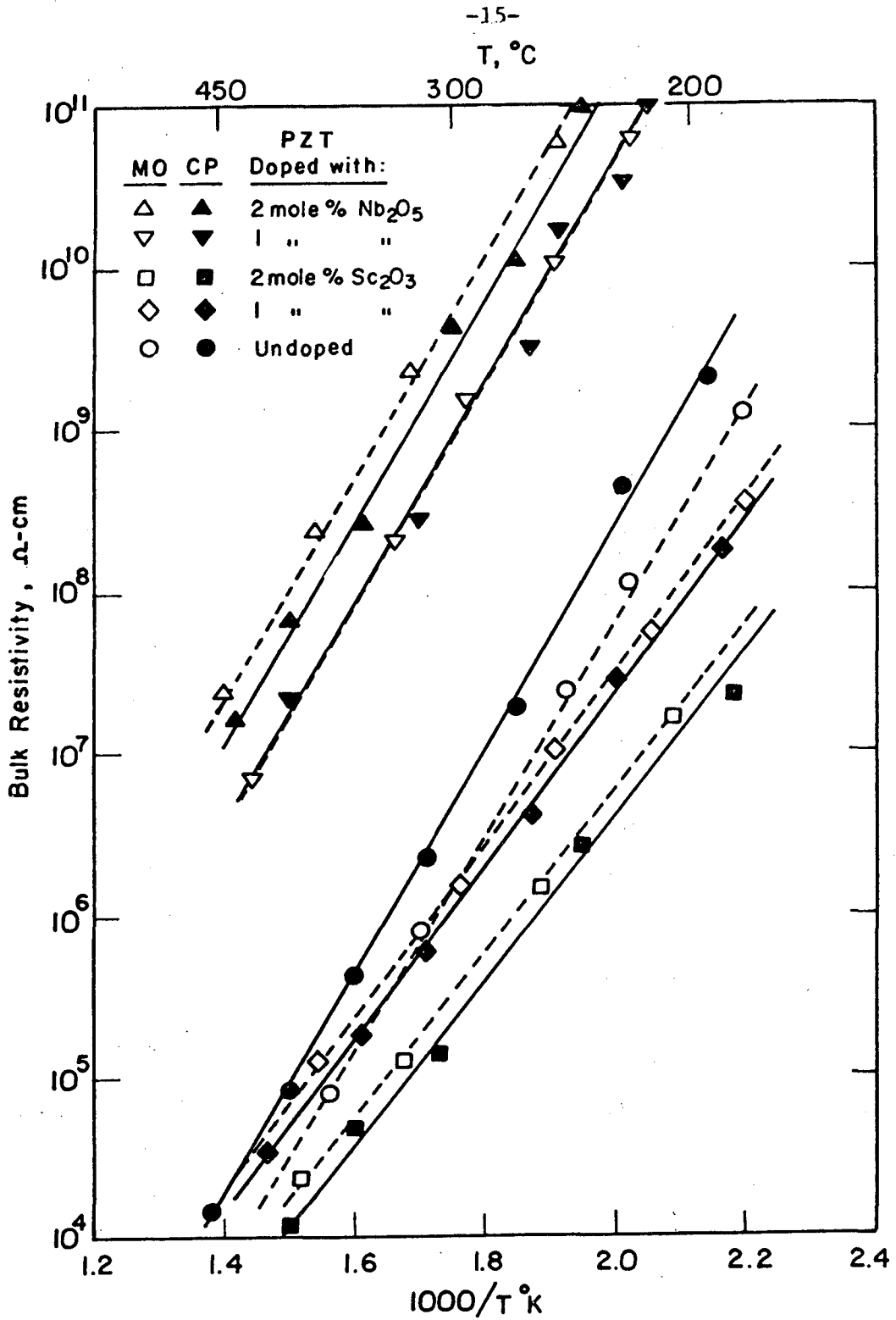
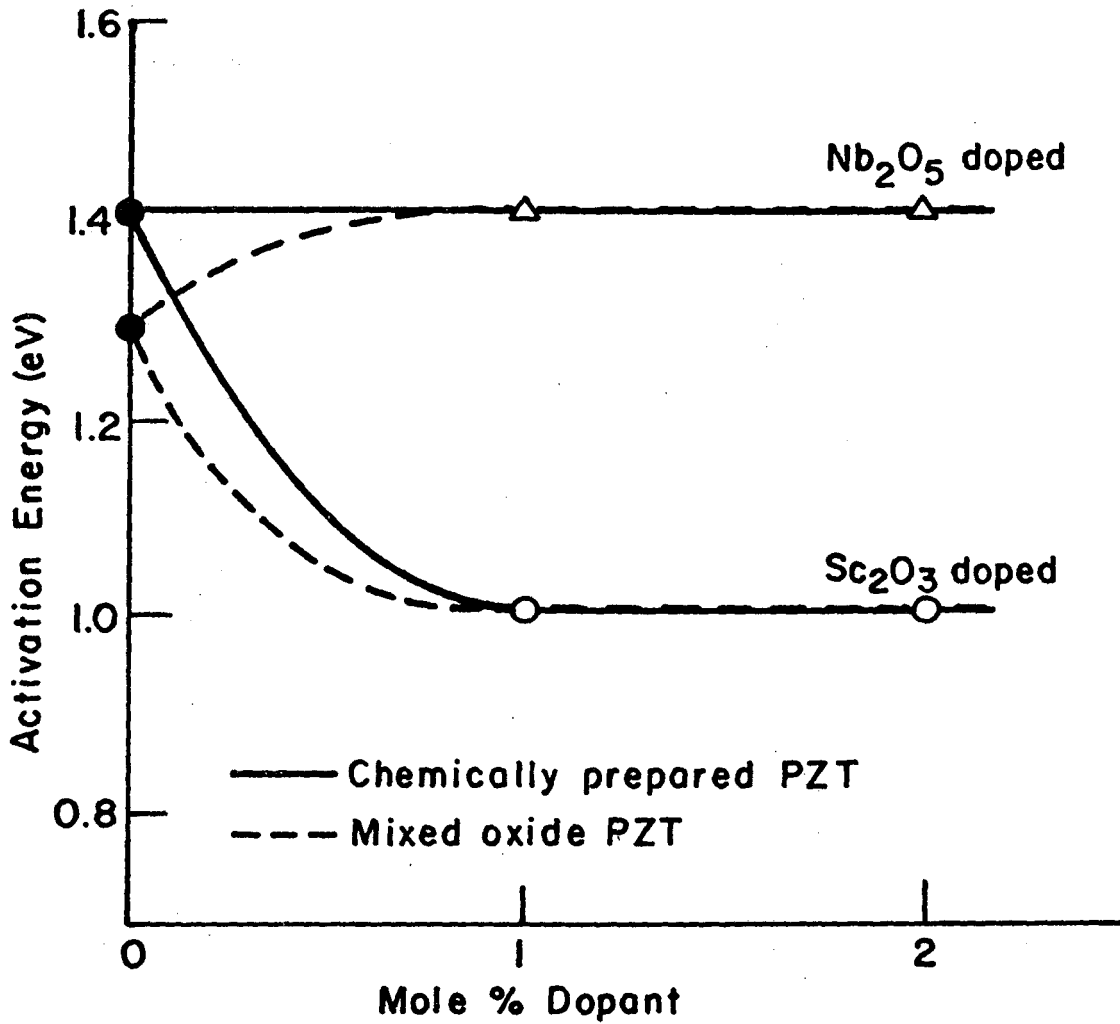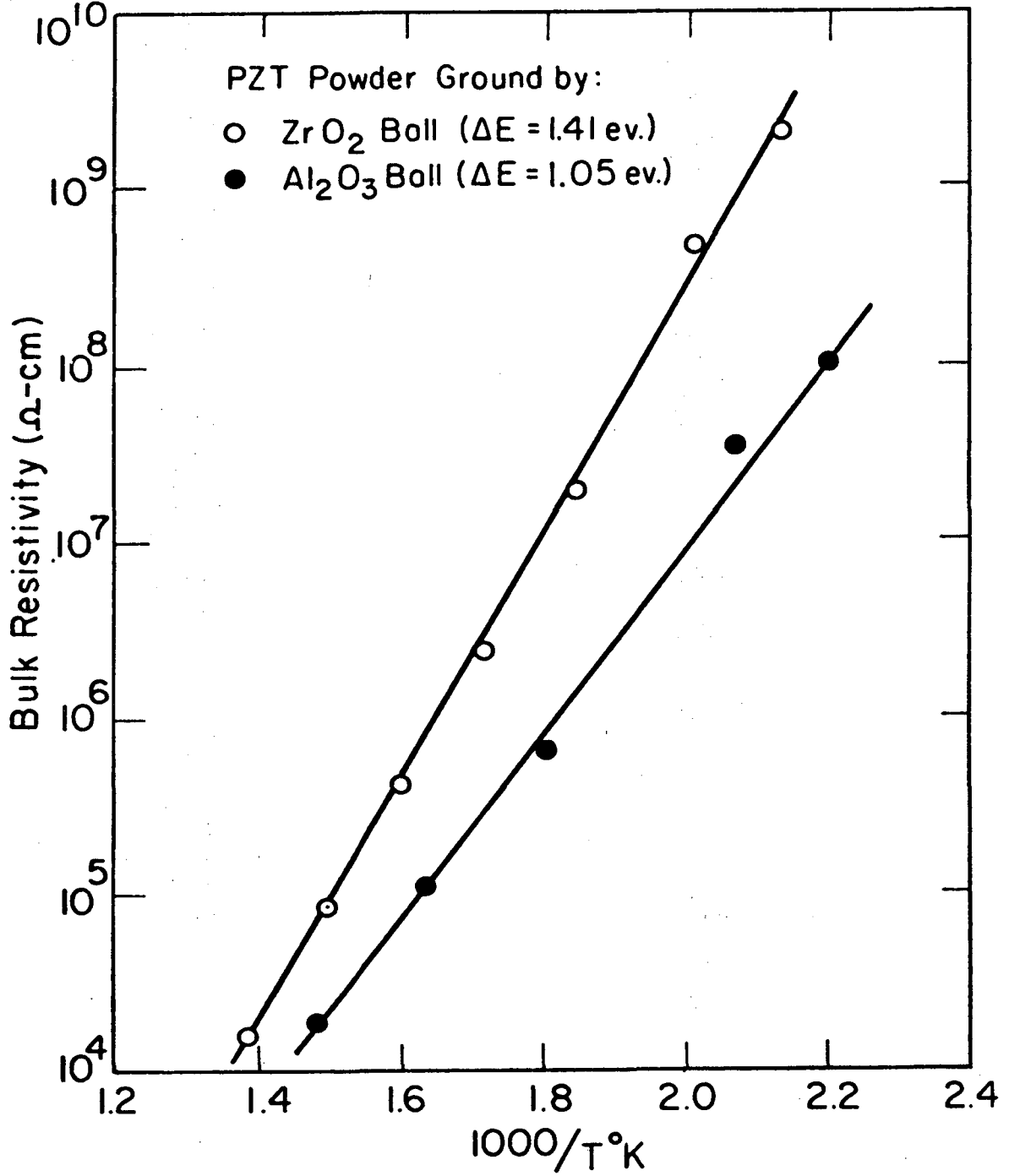$$Pb\,(Zr_{0.5}Ti_{0.5})_{1-X}\,Sc_X\,O_{3-\frac{X}{2}}\,\square_{\frac{X}{2}}$$
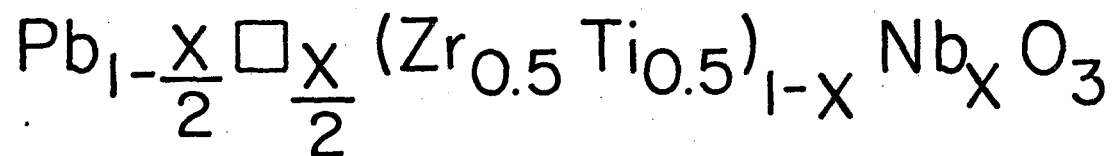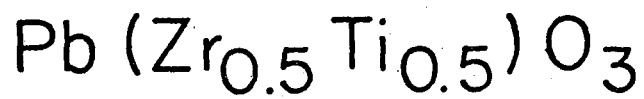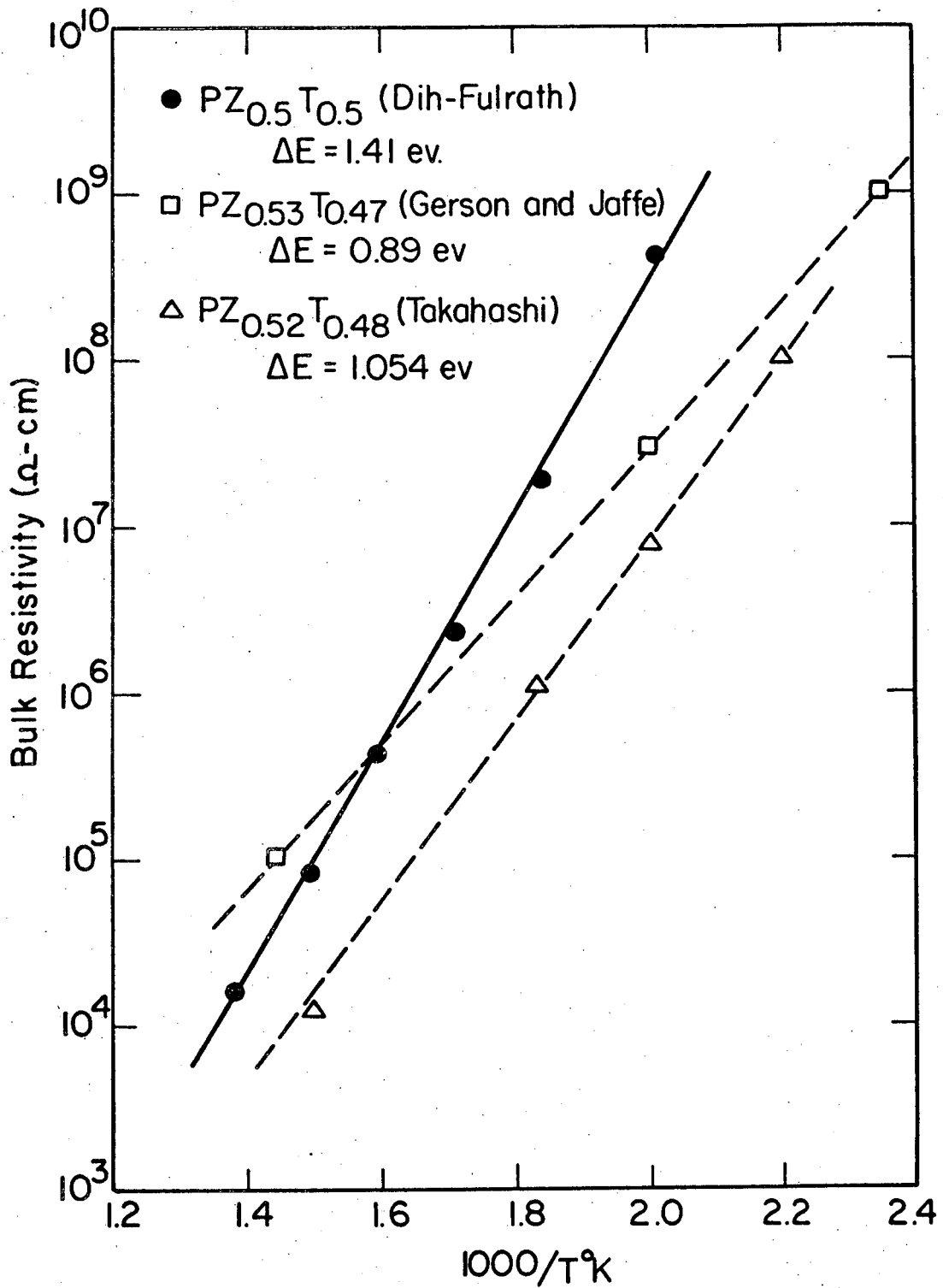
XBL 759-7357

Fig. 3

XBL762-6471

Fig. 4

XBL 759-7363

Fig. 5

Fig. 6

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