

Influence of donor co-doping by niobium or fluorine on the conductivity of Mn doped and Mg doped PZT ceramics

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Abstract

In this study, ac and dc conductivity measurements were performed under ambient atmosphere on doped lead zirconate titanate (PZT) ceramics in order to investigate the defect chemistry by identifying the predominant charge carriers. The considered compositions were acceptor (1% mol Mn or Mg) and donor (Nb or F) co-doped PZTs with [Donor] = 1 or 2% mol.

The influence of donor concentration on the conductivity was determined. From the conduction activation energy values calculated in the temperature range 200–700 °C, the principal contributing charge carriers are doubly-ionized oxygen V_{O} and lead vacancies V_{Pb} . For Mg doped PZTs, neither Nb nor F co-doping strongly reduce both conductivity levels and the dominant conducting species V_{O} . For Mn doped materials, both donor co-dopants niobium and fluorine reduce the conductivity but do not have the same effect on the conduction mechanism at low temperature. With 2% Nb doping, the dominant conducting species are V_{O} whereas electrical conduction is controlled by electrons from the second-ionization of oxygen vacancies with 2% F doping. The difference of oxygen vacancies content in (Mn, F) and (Mn, Nb) co-doped PZTs may be at the origin of the two distinct conducting species and of the different conductivity levels.

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1. Introduction

Lead zirconate titanate ceramics of general formula $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (abbreviated PZT) are well-known piezoelectric materials. During the last fifteen years,¹ a new family of co-doped PZT ceramics has been developed with an acceptor dopant in B site and fluorine as a donor dopant. Fluorine has a valence of -1 and an ionic radius (0.133 nm) equal to that of O^{2-} . These PZTs exhibit both high piezo activity and high mechanical quality factor; in fact, the characteristics strongly depend on the valence of the acceptor which is Mg or Mn. Recently,² it has been demonstrated that (Mn, F) co-doped PZTs and (Mn, Nb) co-doped PZTs present quite similar room temperature piezo characteristics for a same content of donor dopant. This result is expected by considering that both Nb^{5+} and F^- ions bring the same amount of positive extra charges to the lattice since they replace constitutive ions of

valence $+4$ ($\text{Zr}^{4+}/\text{Ti}^{4+}$) and valence -2 (O^{2-}) respectively. However, the doping mechanism may be different with B-site donor or anionic site donor dopants. Hence, the purpose of this study is to investigate through electrical conductivity measurements the compensation mechanism which ensures electro-neutrality in acceptor (Mn or Mg) and donor (Nb or F) co-doped PZTs. It is well known that electrical conductivity is often used to determine the defect chemistry and doping mechanism in oxide-based materials. As a matter of fact, the possible conducting carriers may be distinguished by the conduction activation energy values given in the literature.

2. Experimental procedure

The PZT powder was prepared by coprecipitation in a aqueous solution of oxalic acid. Experimental details are given elsewhere.³ Fluorine was added to the precursors powder obtained after coprecipitation through PbF_2 powder.¹

The chosen base composition was $\text{Pb}_{0.89}(\text{Ba}, \text{Sr})_{0.11}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ doped with 1% mol Mg or Mn and/or

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1–2% mol F or Nb. Cationic dopants were added to the solution before coprecipitation as acetates (Mn, Mg) and oxychloride (NbOCl_5). The resulting powders were pressed into discs and the green pellets were sintered at 1230 °C.

For the electrical measurements, disc-shaped ceramics (16 mm diameter, 2 mm thickness) were electroded with silver paste fired at 700 °C. Conductivity measurements were made using complex impedance spectroscopy⁴ in the temperature range 200–700 °C. The temperature was read with an accuracy of ± 0.5 °C. Impedance data (real Z' and imaginary Z'' components) were collected at a constant temperature using an impedance analyzer (HP 4194 A) in the frequency range of 100 Hz to 1 MHz with an applied voltage of 1 V. Bulk dc resistance values were extracted from complex plane plots (Z'' versus Z') or spectroscopic plots (Z'' versus $\log(f)$). When the temperature was too low to give rise to a semicircle in Z^* plots and to a Debye peak in $Z''(f)$ plots, bulk dc resistance was measured with a Keithley-617 electrometer. The optical absorption of some PZT compositions was measured with UV/Vis spectrometer Lambda 35 (Perkin Elmer).

3. Results and discussion

3.1. Conductivity of Mg doped PZTs

Fig. 1 shows the Arrhenius plots of bulk conductivity of (Mg, F) and (Mg, Nb) co-doped PZT ceramics respectively. Whatever the type of donor dopant used and its concentration, every PZT exhibit roughly the same temperature dependence and donor co-doping makes conductivity values decrease a little for a given temperature.

For (Mg, F) PZTs, the calculated activation energies for conduction lie in the range 1.05–1.18 eV ($E_a = 1.05$ eV for only Mg-doped PZT). Concerning (Mg, Nb) PZTs, E_a is about 1.05–1.25 eV. These ranges of E_a values is very close to the activation energy value (1–1.1 eV) of the ionic conductivity by doubly-ionized oxygen vacancies V_{O} in perovskite-type ferroelectric oxides reported by many authors, like Waser⁵ and Raymond.⁶ Besides, these defects are known to

be the most mobile ionic species in the perovskite lattice. So, it can be concluded that between 200 °C and 700 °C the conducting species in (Mg, F) and (Mg, Nb) specimens are V_{O} . These anionic defects appear to charge compensate the electrical unbalance caused by acceptor dopant Mg^{2+} although it could be theoretically compensated by the extra positive charges brought by 2% mol F^- and Nb^{5+} without the need of oxygen vacancies. However, it is clear that both F and Nb co-doping in Mg doped PZTs have not a strong influence on the conductivity level of the ceramics.

3.2. Conductivity of (Mn, Nb) co-doped PZTs

Fig. 2 shows the Arrhenius dependence of bulk conductivity data of (Mn, Nb) PZTs. It clearly appears that Nb co-doping makes the conductivity decrease monotonously and to a greater extent than for Mg doped PZTs. Besides, different temperature-dependent behaviours are observed: the Arrhenius plot of only Mn doped PZT presents one slope (i.e. activation energy) between 200 and 700 °C whereas (Mn, 1% Nb) and (Mn, 2% Nb) PZTs exhibit one and two slope changes respectively, which means that different conduction mechanisms are activated depending on the temperature range. Fig. 2 also gives the activation energy values of (Mn, Nb) PZTs.

The activation energies for conduction are about 0.93–1.18 eV ($E_a = 1.18$ eV for only Mn-doped PZT) in the low temperature region (200–~330 °C). So, the conductivity is attributed to the doubly-ionized oxygen vacancy hopping, even for the heavily donor doped PZT (1% Mn, 2% Nb). The presence of V_{O} is expected in only Mn doped PZT to ensure electro-neutrality because Mn is predominantly in valence +3.² However, the presence of such defects is not obvious in (1% Mn, 1% Nb) specimen because the default of positive charges induced by one Mn^{3+} ion could be theoretically compensated by one donor Nb^{5+} ion. These defects are also unexpected in (1% Mn, 2% Nb) PZT which is electrically neutral thanks to every Mn ions in valence +2 or to lead vacancies. In fact, recent electron paramagnetic resonance measurements

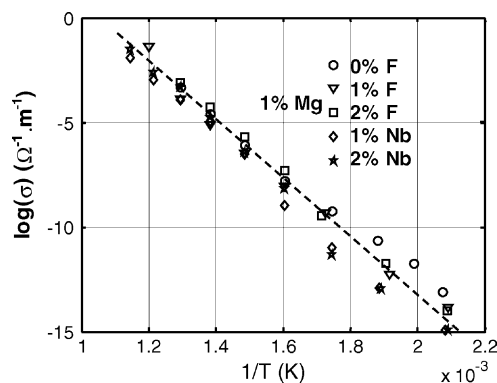


Fig. 1. Arrhenius plot of the conductivity of (Mg, F) and (Mg, Nb) co-doped PZTs. Only one straight line has been drawn to keep the figure clear.

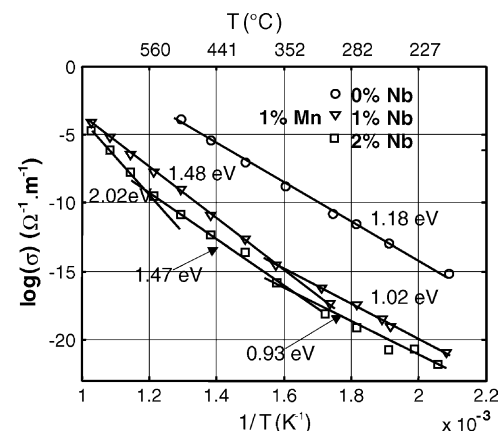


Fig. 2. Arrhenius plot of the conductivity of (Mn, Nb) co-doped PZTs.

have revealed that even after Nb co-doping, Mn^{2+} and Mn^{4+} exist at very low concentration, so Mn^{3+} still predominates (E. Boucher, personal communication). Whatever, the present experiment shows that a small amount of oxygen vacancies is maintained in (Mn, Nb) co-doped PZTs. In the moderate temperature region ($\sim 330\text{--}500\text{ }^\circ\text{C}$) where the low temperature limit corresponds to the first slope change in the Arrhenius plot for (Mn, 1% Nb) and (Mn, 2% Nb) PZT, these PZTs exhibit the same activation energy (1.47–1.48 eV). This value is assigned to a mixed conduction mechanism by doubly-ionized oxygen vacancies and lead vacancies V_{Pb} diffusion. Although Pb vacancies are quenched defects at low temperature which are difficult to activate, they become mobile above $300\text{ }^\circ\text{C}$ and the magnitude of E_a ($\sim 1.5\text{ eV}$) indicates that they contribute to the conduction in addition to the oxygen vacancy conduction. In the heavily donor doped PZT (1% Mn, 2% Nb), there are more Pb vacancies than the other PZTs of the series. Thus, in the high temperature regime (above $\sim 500\text{ }^\circ\text{C}$, i.e. second slope change in the Arrhenius plot) Pb vacancies become predominant conducting ionic species with a corresponding E_a value of 2.02 eV, which is in good agreement with the value of 1.95 eV found by Peláiz Barranco et al in heavily La doped PZT.⁷

3.3. Conductivity of (Mn, F) co-doped PZTs

The Arrhenius plots of conductivity of (Mn, F) PZTs are shown in Fig. 3. As for Nb co-doping, F co-doping reduces the conductivity level of Mn doped PZTs but to a less extent for a given donor content, especially for 2% mol F. The characteristics of the conductivity process for the different (Mn, F) samples are also given in the figure.

Conductivity due to V_{O} is observed for (1% Mn, 1% F) specimen ($E_a = 1.08\text{ eV}$) in the low temperature region $200\text{--}330\text{ }^\circ\text{C}$. As for (1% Mn, 1% Nb) PZT, one Mn^{3+} ion could be compensated by one F^- anion but oxygen vacancies are still present. A lower activation energy is found for (Mn, 2% F) co-doped ($E_a = 0.65\text{ eV}$) between 200 and $390\text{ }^\circ\text{C}$. This is also the case for the PZT co-doped with 3% F ($E_a = 0.70\text{ eV}$,

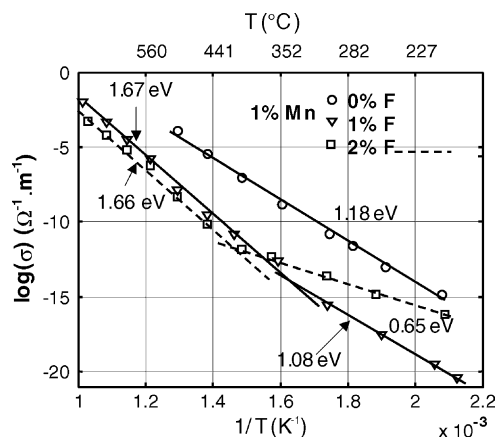


Fig. 3. Arrhenius plot of the conductivity of (Mn, F) co-doped PZTs.

data not shown). This value has already been reported by Ang et al.⁸ for the electrical conduction of Bi doped SrTiO_3 ceramics between 77 and $327\text{ }^\circ\text{C}$ under air. These authors considered that the conduction carriers were electrons from the second ionization of oxygen vacancies generated, according to the following equation with a corresponding energy of $E_d = 1.4\text{ eV}$:



Thus, we could reasonably suggest that electrons control the conductivity process in the (Mn, 2% F) PZT at low temperature. In the high temperature region, mixed conduction governed by both doubly ionized oxygen and lead vacancies appear for 1% F and 2% F co-doped PZTs ($E_a \sim 1.66\text{ eV}$). Surprisingly, the 2% F co-doped sample does not exhibit an intermediate temperature range in which conductivity is ensured only by V_{O} (with an E_a close to 1 eV), whereas these defects are certainly present from Eq. (1).

3.4. Optical absorption measurements

Room temperature (RT) optical absorption measurements have been performed to determine if different ionization states of oxygen vacancies could be confirmed in the doped PZTs. Fig. 4 shows the optical spectra of only Mg, only Mn, (Mg, 2% F), (Mn, 2% Nb) and (Mn, 2% F) co-doped PZTs.

For every PZTs, two broad peaks are observed, one peak corresponding approximately to the band gap ($E_g \sim 3.2\text{ eV}$) and the second peak at $\sim 1.3\text{ eV}$, energy value close to second-ionization energy of V_{O} . This peak is attributed to the energy level associated with two electrons trapped at an oxygen vacancy.⁸ It is clear that it is more intensive for the Mn, 2% Nb and 2% F co-doped PZTs than for donor undoped PZTs or (Mg, 2% Nb or F) co-doped. This indicates that singly-ionized oxygen vacancies are relatively more numerous in these samples than in donor undoped PZTs or (Mg, 2% Nb or F) co-doped in which the main part of oxygen vacancies is already doubly-ionized at RT. Finally, the RT optical results are in good agreement with the electrical response attributed to V_{O} in only acceptor doped and (Mg, donor) co-doped specimens, it also confirms that high donor

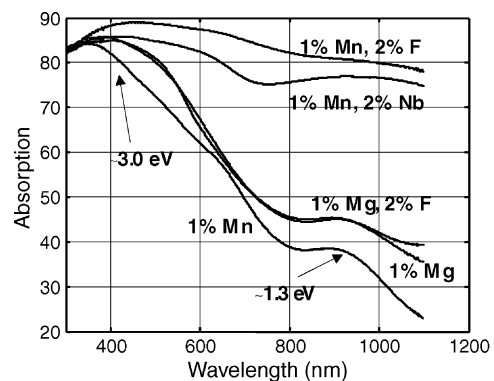


Fig. 4. Room temperature optical absorption spectra of some doped PZTs.

doping thermally stabilizes singly-ionized V_{O} in (Mn, donor) co-doped. However, the difference of conductivity process at low temperature between (Mn, 2% Nb) and (Mn, 2% F) PZTs remains unclear. In fact, (Mn, 2% Nb) PZT should exhibit the same temperature-dependent behaviour as (Mn, 2% F), but it does not. It is believed this is due to the oxygen vacancy content less important in Nb co-doped PZT. This assumption would be confirmed by the higher resistivity of (Mn, 2% Nb) in the whole studied temperature range.

4. Conclusions

In this paper, conductivity measurements have been performed in the temperature range 200–700 °C on (Mg or Mn, Nb or F) co-doped PZTs. The principal objective was to determine the defect chemistry in these ceramics thanks to the identification of the possible charge carriers through activation energies. The study revealed that:

- For Mg doped PZT, neither Nb nor F co-doping strongly influence both conductivity levels and the dominant conducting species which are V_{O} .
- For Mn doped PZT, both Nb and F co-doping reduce the conductivity significantly. However, F co-doped PZTs are more conducting than Nb co-doped ones and different temperature-dependent mechanisms are observed. At low temperature, electrical conduction in (Mn, Nb) PZTs is mainly governed by V_{O} , even for heavily Nb co-doped sample, whereas electrons from the second-ionization of the oxygen vacancies are the conducting species in 2% F

co-doped PZT. At high temperature, whatever the donor, V_{O} and V_{Pb} vacancies remain the dominant charge carriers which diffusion in the lattice by hopping controls the conduction. Finally, whatever the pair of co-dopants used, an ionic compensation mechanism by vacancies always occurs even if it is found that Nb co-doping reduces the oxygen vacancies content.

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