Oxidation kinetic study of copper(I) in ferroelectric ceramic [PbTiO$_3$-PbZrO$_3$-PbCuNbO$_3$ + 0.5 mol%MnO$_2$] system by high resolution thermogravimetric analysis

E. Torres García[a,*], A. Peláiz Barranco[b], C. Vázquez[c],
F. Calderón Piñar[b,d], O. Pérez Martínez[b]

[a]*Facultad de Química-Instituto de Materiales y Reactivos, Universidad de La Habana, Zapata y G, Vedado, La Habana 10400, Cuba*
[b]*Facultad de Física-Instituto de Materiales y Reactivos, Universidad de La Habana, San Lázaro y L, Vedado, La Habana 10400, Cuba*
[c]*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, A.P. 70-360 Mexico D.F. 04510, Mexico*
[d]*Centro de Investigaciones en Ciencia Aplicada y Tecnología de Avanzada (CICATA)-Altamira, Altamira, Tamps, Mexico*

Abstract

The Cu$^+$ oxidation reaction study in the PbZr$_{0.50}$Ti$_{0.44}$(Cu$_{1/4}$Nb$_{3/4}$)$_{0.06}$O$_3$ + 0.5 mol%MnO$_2$ ferroelectric ceramic was carried out using high-resolution themogravimetry (Hi-Res TGA) and the kinetic analysis was made by using the traditional criterion of the mathematical fitting of $f(\alpha)$ functions and the isoconversion method. A D2 diffusion mechanism with a variable activation energy value in the range 75–103 kJ/mol was obtained and the results were interpreted in two ways: an inter-crystallite oxygen diffusion and a copper(I) oxidation process. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Modified lead titanate zirconate ceramics (PZT) are studied extensively owing to their excellent properties for practical applications [1]. A particular modification, PbZr$_{0.50}$Ti$_{0.44}$(Cu$_{1/4}$Nb$_{3/4}$)$_{0.06}$O$_3$, have been investigated previously in pure state and with addition of 0.5 mol%MnO$_2$ [2,3] in order to evaluate the influence of the manganese addition. It is a ferroelectric ternary system where copper and niobium ions replace the Zr^{4+} or Ti^{4+} in B sites of the structure as hard and soft doping ions, respectively. This system

has exhibited a gradual increment of the dielectric losses with the temperature and a little relative maximum at Curie point (343°C), behavior that are suggested an undesirable ohmic conductivity associated with the mobile particles. The temperature programmed reduction measurements (TPR) in H$_2$ atmosphere have shown the presence of Cu$^+$ [4] which must exhibit a reversible oxidation process to Cu^{2+} in air condition, which are the normal measurement conditions for the electric, dielectric and ferroelectric characterization. On the other hand, a lower contribution to the conductive mechanisms is obtained in manganese doped system than that of undoped ceramic from Cu$^+$ oxidation process, which induces a higher resistivity values in the Mn-doped case. These results have shown the needed of the oxidation kinetic

* Corresponding author. Fax: +53-7-335774.
E-mail addresses: etorres@imre.oc.uh.cu, pilc@xanum.uam.mx
(E. Torres García).

study of copper in the ceramic in order to explain its electrical behavior associated to the copper ions.

This paper presents the analyses carried out on the oxidation process of Cu^+ in $PbZr_{0.5}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3 + 0.5$ mol%MnO_2 (PZT-PCN) system by TGA studies based on conventional constant heating rate TGA and the isoconversion method.

2. Experimental

The composition $PbZr_{0.5}Ti_{0.44}(Cu_{1/4}Nb_{3/4})_{0.06}O_3 +0.5$ mol%MnO_2 (PZT-PCN) was prepared by the hot pressing technique [1,2]. The calcination and milling were carried out simultaneously using a ball mill kept at $600°C$. Hot pressed ceramics were sintered at $1000°C$ for 1 h under a pressure of 6 MPa.

Thermal analyses were done in flow of air (100 ml/min) in a high-resolution thermobalance (TA Instrument, mod. TG-2950). The heating rates were 10 and $20°C$/min and the resolutions used were five. High-resolution themogravimetry (Hi-Res TGA) incorporates basic elements of the techniques conventional and the ideas set by Rouquérol [5–7], and Paulik and Paulik [8,9]. That allows a predefined temperature program to be followed in ranges where there is no modification in the solid, where as in presence of changes in the control property the temperature program adjusts so the prescribed requirement is fulfilled. Then direct information about the kinetics oxidation process could be obtained from the shape of the temperature versus time curve in Hi-Res TGA.

3. Results and discussion

Fig. 1A and B shows the Hi-Res TGA analysis of the ferroelectric ceramic. It can be observed that the sample is gradually and continuously oxidated between 400 and $700°C$, process that takes place in one-step reaction. This has been associated with the process of Cu^+ oxidation in the ferroelectric ceramic in air atmosphere which is an experimental condition for the electrical and ferroelectrical analysis of the ceramic material [4]. Taking account into the stoichiometric analysis of the studied reaction has been stated that there is a total Cu^+/Cu^{2+} oxidation process, i.e.
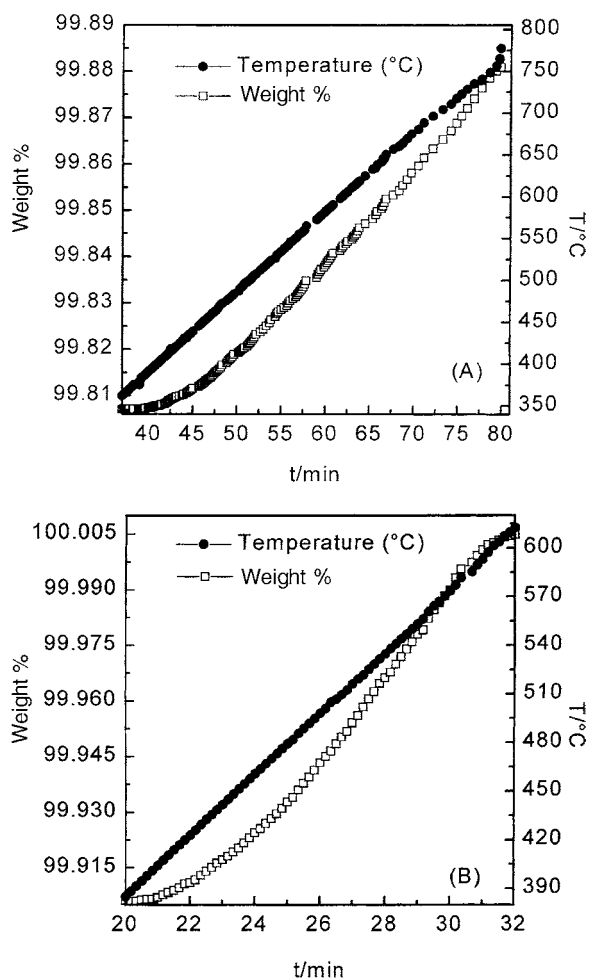

Fig. 1. Hi-Res TGA experimental curves for $10°C$/min (A) and $20°C$/min (B), in PZT-PCN ferroelectric ceramic system.

the enter of oxygen guarantees the stoichiometric oxidation of copper.

4. Oxidation kinetic

In a solid-state reaction for different processes, the evaluation of mass change (α) can be defined as

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{1}$$

where W_0, W and W_f are the initial, actual and final sample masses, respectively.

The rate of reaction depends upon the conversion, according to the general equation

$$\frac{d\alpha}{dt} = k f(\alpha) \tag{2}$$

where $f(\alpha)$ is a function depending on the kinetic model obeyed by the reaction and the rate constant k is frequently assumed to obey the Arrhenius law

$$k = A \, \exp\left(\frac{-E_a}{RT}\right) \tag{3}$$

where A is the pre-exponential factor, E_a the apparent activation energy, R the gas constant and T the absolute temperature. Normally several basic functions, derived by assuming simply idealized models, are used for the kinetic study of the solid-state reactions (Table 1).

If the loss or gain of mass increases as a linear function of time, i.e. $d\alpha/dt = C$ (constant), then Eqs. (2) and (3) can be rearranged

$$\frac{C}{A} = \exp\left(\frac{-E_a}{RT}\right) f(\alpha) \tag{4}$$

where we have thought logarithms, in the form

$$\ln(f(\alpha)) = \frac{E_a}{RT} + \ln\left(\frac{A}{C}\right) \tag{5}$$

Thus, assuming that the term $\ln(A/C)$ is a constant, plots of $\ln(f(\alpha))$ versus reciprocal temperature $1/T$ for various functions $f(\alpha)$ should be linear, having a slope E_a/R. This shows that it is possible to obtain the activation energy value from a single Hi-Res TGA experiment. Fig. 2 shows the temperature dependence of α, obtained at two different heating rates (10 and 20°C/min) over the range $0.05 \le \alpha \le 1$.
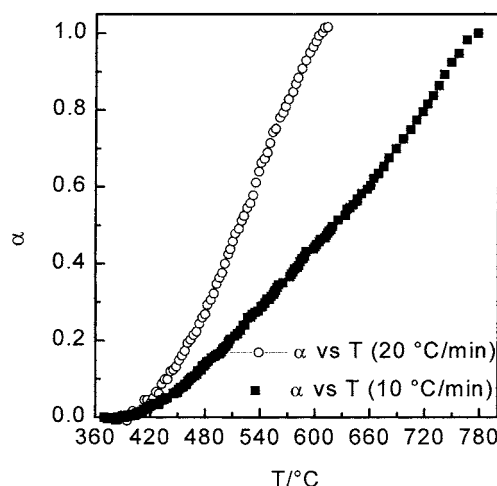

Fig. 2. Experimental α–T plots for the oxidation process of Cu^+ to 10 and 20°C/min.

This profile has a very interesting feature and important information for the elucidation of this oxidation mechanism comparing with theoretical curve reported [10,11]. These results allow correlating the curve shape with the diffusive mechanisms. On the other hand, the analysis made from the respective $f(\alpha)$ functions showed the best correlation coefficients for the diffusion laws (Tables 2 and 3) which are plotted in Fig. 3A and B according to Eq. (5). The other $f(\alpha)$ basic functions (Table 1) did not satisfactorily represent the data.

Taking account that the correlation coefficients are close to 1 and that the difference between these four diffusion models is very little, the oxidation reaction followed by a diffusion law, cannot be evaluated adequately from these representations. Then, the oxidation processes can not be explained completely by

Table 1
Function ($f(\alpha)$) for the most common mechanisms in heterogeneous kinetic (from [10–12])

Model	Symbol	$f(\alpha)$
One-dimensional diffusion	D1	$1/2\alpha$
Two-dimensional diffusion	D2	$-1/\ln(1-\alpha)$
Three-dimensional diffusion (Jander)	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{1/3}]$
Three-dimensional diffusion (Ginstring–Brounshtein)	D4	$3/2[(1-\alpha)^{-1/3}-1]$
Unimolecular decay	F1	$(1-\alpha)$
Phase boundary controlled	R_n $(1 \le n \le 3)$	$n(1-\alpha)^{1-(1/n)}$
Nucleation and growth (Avrami–Erofeev)	A_m $(0.5 \le m \le 4)$	$m(1-\alpha)[-\ln(1-\alpha)]^{1-(1/m)}$

Table 2
Results obtained from the analysis of Eq. (5) for Cu^+ oxidation process in the ferroelectric ceramic at 10°C/min[a]

Mechanism symbol	r	i	S.D.	E_a
D1	0.9964	−5.46	0.031	41
D2	0.9986	−12.23	0.027	91
D3	0.9949	−8.54	0.068	75
D4	0.9959	−8.42	0.057	70

[a] The parameters r, i, S.D. and E_a are the correlation coefficient, the intercept value, the standard deviation and the activation energy (kJ/mol), respectively.

Table 3
Results obtained from the analysis of Eq. (5) for Cu^+ oxidation process in the ferroelectric ceramic at 20°C/min[a]

Mechanism symbol	r	i	S.D.	E_a
D1	0.9948	−10.99	0.044	72
D2	0.9993	−15.16	0.022	101
D3	0.9969	−19.32	0.063	136
D4	0.9977	−18.39	0.050	126

[a] The parameters r, i, S.D. and E_a are the correlation coefficient, the intercept value, the standard deviation and the activation energy (kJ/mol), respectively.

this way. In order to makes it possible, the analysis at different oxidation rates has been carried out. The Eq. (5), at two-oxidation rates, to isoconversion $\alpha_1 = \alpha_2$, can be expressed as

$$\ln(f(\alpha)) = \frac{E_a}{RT_1} + \ln\left(\frac{A}{C_1}\right) \qquad (6)$$

and

$$\ln(f(\alpha)) = \frac{E_a}{RT_2} + \ln\left(\frac{A}{C_2}\right) \qquad (7)$$

where C_1 and C_2 are the two decomposition rates ($d\alpha/dt$) corresponding to the temperature T_1 and T_2, respectively. Then the activation energy can be expressed as

$$E_a = R \ln \frac{C_2/C_1}{(1/T_1) - (1/T_2)} \qquad (8)$$

Thus, the E_a-values can be estimated without previous knowledge of the actual reaction mechanism. Based on the free kinetic model [13], it is possible to obtain information about the mechanism of a process and
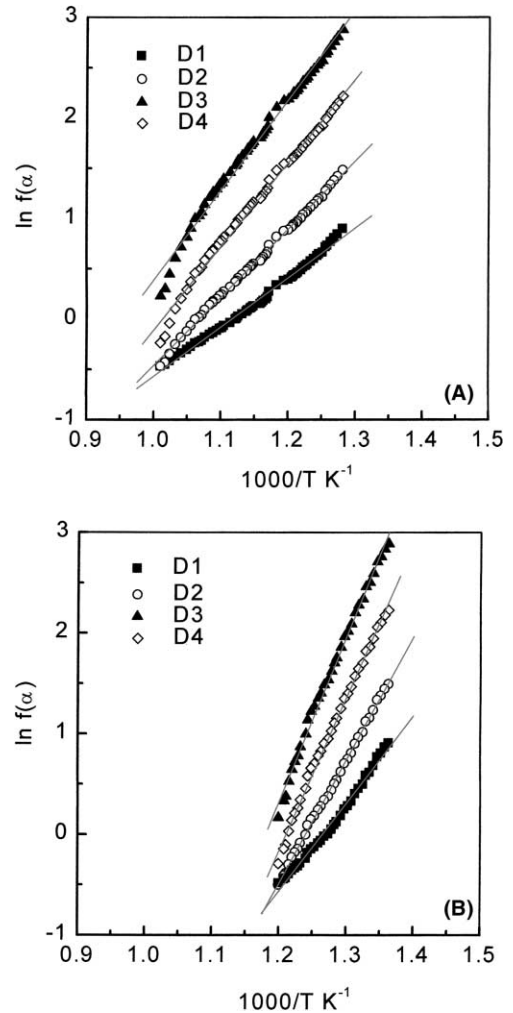

Fig. 3. Temperature dependence of $\ln f(\alpha)$ for the diffusion models at 10°C/min (A) and 20°C/min (B), in the PZT-PCN ferroelectric ceramic.

predict its kinetic without the knowledge of both the reaction model and the pre-exponential factor. Fig. 4 shows the E_a-values analyzed from Eq. (8) by the isoconversion method.

These results show a complex E_a–α dependence: a characteristic behavior for a reaction complicated by diffusion up to $\alpha = 0.55$, according to Vyazovkin and coworkers [13–18], and a variation in the $E_a(\alpha)$ slope which could be associated to a change in the reaction mechanism.

From these analysis we could evaluate the Cu^+ oxidation process in the PZT-PCN ferroelectric
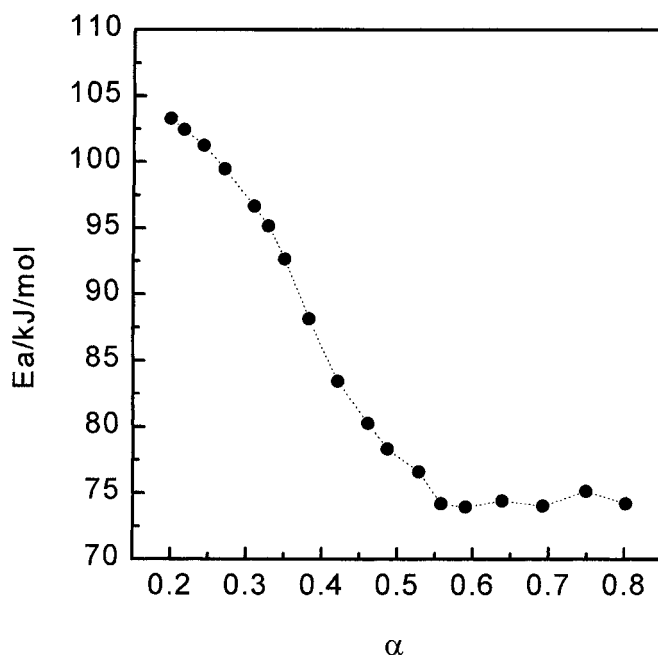
Fig. 4. Results obtained from the representation of Eq. (8) by the isoconversion method.

ceramic showing predominant diffusive mechanisms. On the other hand, it was observed a linear temperature dependence of the reaction rate which is associated with diffusion at surface scale [19]. It could be interpreted as a limited reaction rate by the inter-crystallite diffusion of the oxygen in the solid system.

It has been established the limitations of the classical model of mathematical fitting of the $f(\alpha)$ functions to discriminate the kinetic law. Therefore, it was necessary to compare the energy activation results obtained by this method and the isoconversion method. The best kinetic law would be which gives the best correlation coefficient and the best agreement between the E_a-value calculated as above and the value measured directly and independently by the isoconversion method. Then, the most probably mechanism that describes the Cu^+ oxidation process in the PZT-PCN system is D2 (bidimensional diffusion) with an activation energy value in the range 75–103 kJ/mol, characteristic range for controlled processes by a diffusion-reaction (50–150 kJ/mol) [19]. This is a good criterion taking into account that together with the diffusion there is an oxidation processes at the particle surface. The decrement of the activation energy value with the increment of the

transformation rate α and with the decrement of heating rate, for the isoconversion and mathematical methods, respectively, is associated with the temperature dependence of the reaction degree α and the autocatalytical characteristics of the reaction.

5. Conclusions

The Cu^+ oxidation reaction kinetic analysis in the PZT-PCN ferroelectric ceramic was carried out by the traditional criterion of the mathematical fitting of $f(\alpha)$ functions and the isoconversion method to determinate the Arrhenius kinetic parameters and the reaction mechanisms. A D2 diffusion mechanism with a variable activation energy value in the range 75–103 kJ/mol was evaluated and the results were interpreted in two ways: an inter-crystallite oxygen diffusion and a copper(I) oxidation process.

Acknowledgements

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