

Lead hafnate titanate (PHT) ceramics: processing and properties

G. Fantozzi^{a,*}, H. Idrissi^{a,b}, C. Favotto^c, M. Roubin^c

^aGroupe d'Etude de Métallurgie Physique et de Physique des Matériaux, (UMR, CNRS 5510), 20, Av. Einstein, 69621 Villeurbanne Cedex, France

^bUniversité Hassan II- Faculté des sciences Ainchock, Département de physique, Km 8, route d'El Jadida, BP 5366 Maârif Casablanca, Maroc

^cMatériaux à Finalité Spécifique (UPRES No. 1356), Laboratoire de Physico-Chimie du Matériau et du Milieu Marin, BP 132, 83957 La Garde Cedex, France

Received 28 April 1997; received in revised form 28 January 2000; accepted 1 February 2000

Abstract

The aim of the present paper is to investigate the processing and properties of lead hafnium and titanium based ceramic $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ ($x=0.5$), noted PHT. The first part is devoted to processing: powders are obtained from pyrolysis of oxalic precursor. Powder characteristics depend on the used conditions of pyrolysis. They are optimized in order to obtain an easier sintering behaviour. The second part is concentrated on physical properties of PHT such as piezoelectric, dielectric loss and permittivity and on the anelastic behaviour (mechanical loss and elastic modulus). These properties, measured as a function of temperature, allow us to show the presence of two phase transitions and the motion of domain walls in the ferroelectric phase. Furthermore, the dielectric and piezoelectric properties of PHT are similar to the PZT [$\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$] ones. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric properties; Ferroelectric properties; $\text{Pb}(\text{Hf}, \text{Ti})\text{O}_3$; Perovskite; Powders-chemical preparation

1. Introduction

Numerous studies have been conducted on piezoelectric ceramics largely used in technology. These studies concern, essentially, barium titanate, lead zirconate titanate (PZT) and PZT modified by doping. In the morphotropic zone between the rhombohedral and tetragonal phases, the piezoelectric constants of PZT are much larger than the barium titanate ones.¹ So, the PZT ceramics have been intensively investigated.

The zirconium can be substituted by hafnium (largely available): Jaffe et al.² have shown that $\text{Pb}(\text{H}_{0.5}\text{Ti}_{0.5})\text{O}_3$ has the same structural and physical characteristics as the PZT ones. But the PHT ceramics have been less studied comparatively to the PZT ones.^{3–5} The PZT ceramics exhibit high piezoelectric coefficients d_{33} in the range 140–250 pC/N and relative dielectric constant of about 650.³ The PHT properties are not well known and it will be interesting to specify the physical properties of these ceramics.

The purpose of our study is firstly to investigate processing of PHT and secondly to determine the physical properties of the PHT ceramics and so to compare the PHT behaviour to the PZT one.

Concerning processing, powders are prepared from pyrolysis of oxalic precursor and optimized in order to obtain a better sintering behaviour.

To prepare pure oxides, a soft chemical method from an organometallic precursor like oxalate⁶ has been used.

This process allows the valorization of hafnium tetrachlorate, by-product of zirconium production. The thermolysis conditions have an effect on the powder morphology and so on the compaction and densification behaviour of the obtained powder.

After sintering, the following physical properties of PHT have been determined: piezoelectric coefficient, dielectric constant and loss. So, a comparison of the PHT and PZT properties can be made.

Furthermore, the anelastic behaviour of the PHT ceramics has been studied, this technique allowing the study of the phase transitions and of the motion of domain walls in the ferroelectric phases.⁷ Previous studies on PZT have shown that the domain structure and the domain walls influence significantly the dielectric and piezoelectric response of these ceramics.^{8,9}

* Corresponding author.

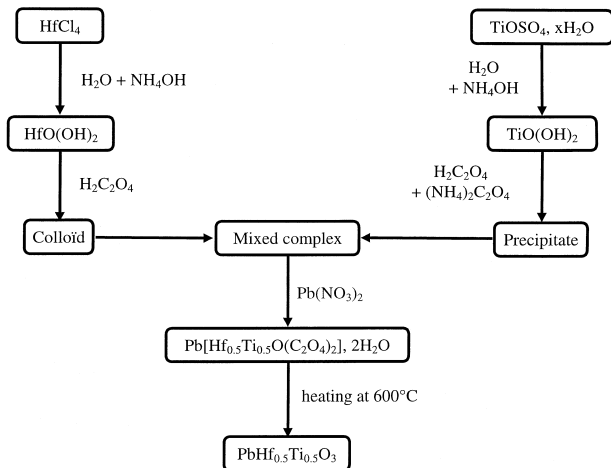
E-mail address: gtmppm@insa.insa-lyon.fr (G. Fantozzi).

2. Processing of PHT ceramics

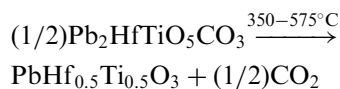
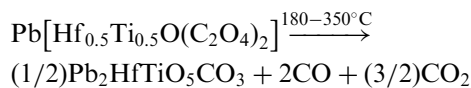
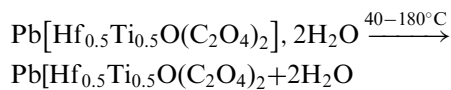
2.1. Powder preparation¹⁰

Titanates, zirconates and hafnates can be prepared by firing appropriate mixtures of oxides, carbonates or nitrates. Generally, materials obtained by this route are not very homogeneous. $\text{PbHf}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PHT) are prepared by a soft chemistry process by decomposition of oxalic precursor. Hafnyl oxalic acid $\text{H}_2[\text{HfO}(\text{C}_2\text{O}_4)]$, $5\text{H}_2\text{O}$ ¹¹ and titanyl oxalic ammonium $(\text{NH}_4)_2[\text{TiO}(\text{C}_2\text{O}_4)_2]$, $2\text{H}_2\text{O}$ ¹² were used in which lead is introduced by reaction with lead nitrate in aqueous medium. An organometallic complex which contains metallic elements in the same proportion as those of the oxide is elaborated. The different steps of the powder preparation are indicated on the schematic diagram below.

The pyrolysis at 600°C of $\text{Pb}[\text{Hf}_{0.5}\text{Ti}_{0.5}\text{O}(\text{C}_2\text{O}_4)_2]$, $2\text{H}_2\text{O}$ precursor gives directly the $\text{PbHf}_{0.5}\text{Ti}_{0.5}\text{O}_3$ oxide.



Decomposition during pyrolysis occurs through the following steps:



The obtained powders are always single-phase.

In order to have an easier sintering, control of particle size distribution can be achieved by controlling the temperature of pyrolysis. So, the oxalic complex has been heated up to the minimum temperature necessary

to obtain the oxide i.e. 600°C in order to have a smaller size granulometric distribution.

The specific surface and the porosity of the powder depend on the heating rate of the mixed complex pyrolysis as shown in Fig. 1. A minimum of porosity has been noticed for a heating rate of 3°C/min.

After preparation, the microstructure of the powder is shown in Fig. 2.

2.2. Sintering

The powder can be compacted by using uniaxial or isotatic pressing. After sintering, no difference in density was noticed after uniaxial compaction or isotatic pressing. So we have only used uniaxial pressing at 80 MPa. Compacted samples have the shape of pellets (10 mm in diameter and 4 mm in thickness) and bars (44×8×4 mm³).

For sintering, the pellets and bars are disposed in an alumina box (Fig. 3) containing PbHfO_3 (or PbZrO_3) and a mixture of $\text{MgO} + \text{PbO}$. The PbHfO_3 (or PbZrO_3) oxide is used for avoiding the PbO loss during the sintering. Magnesium oxide plays a role for the temperature homogenization.

The alumina box is placed in a furnace which is heated up to 1250°C with a heating rate of 5°C/min, maintained at 1250°C during 3 h and naturally cooled¹⁰ (the heating rate and the dwell time has no influence on sintering).

The density of sintered samples was determined by pycnometry. For the above sintering cycle, a density of 8.5 g/cm³ was obtained for PHT ceramics which represents 92% of the theoretical density. A typical microstructure of PHT ceramics is shown in Fig. 4a.

After sintering, spontaneous polarization domains appear (Fig. 4b). The polarisation direction change from one domain to another one is 90 or 180°. During polarization, the domains are oriented.

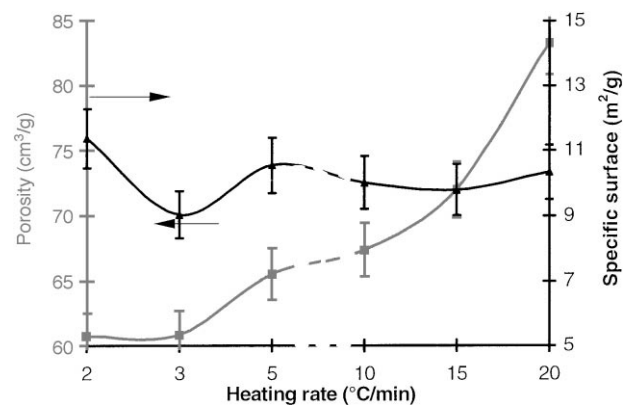


Fig. 1. Evolution of the specific surface and the porosity of the powder versus the heating rate.

2.3. PHT ceramic polarization

The ceramic is set into an electric field of 10 kV/mm in a silicone oil bath heated at 220°C (Fig. 5). When the ceramic is polarized, its piezoelectric properties can be determined

3. Properties of PHT ceramics

3.1. Piezoelectric properties

After polarization, the piezoelectric coefficient d_{33} was measured as a function of temperature from 25 to 350°C by using a Berlincourt apparatus linked to a computer (Fig. 6). The piezoelectric coefficient decreases above 200°C and becomes zero at T_c .

The piezoelectric behaviour of PZT is well known whereas the PHT one has not been studied intensively. A comparison between the piezoelectric coefficients of PHT ceramics and doped or undoped PZT ceramics is shown in Table 1. In the morphotropic zone, the PZT ceramic present a piezoelectric coefficient between 140 and 250 pC/N.⁹

The measured PHT piezoelectric coefficient at room temperature (140 pC/N) is already satisfactory and can be probably improved by a better densification during sintering.

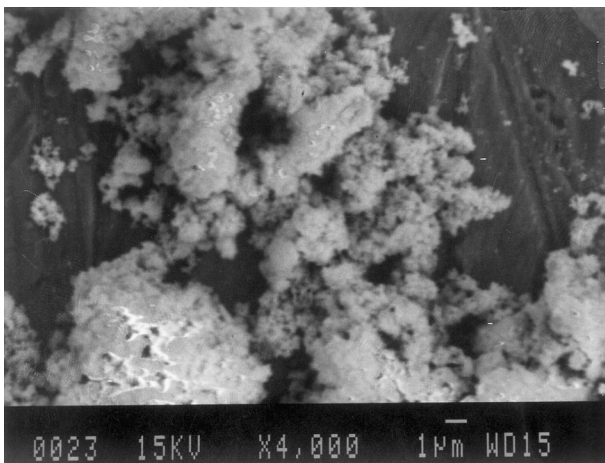


Fig. 2. Scanning electron micrograph of the obtained powder.

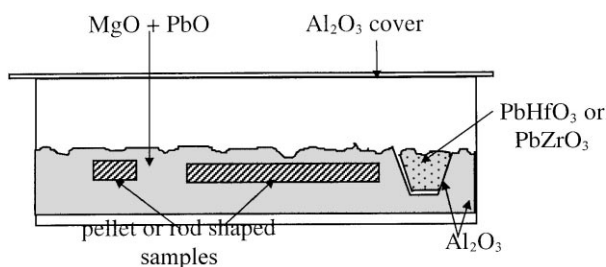


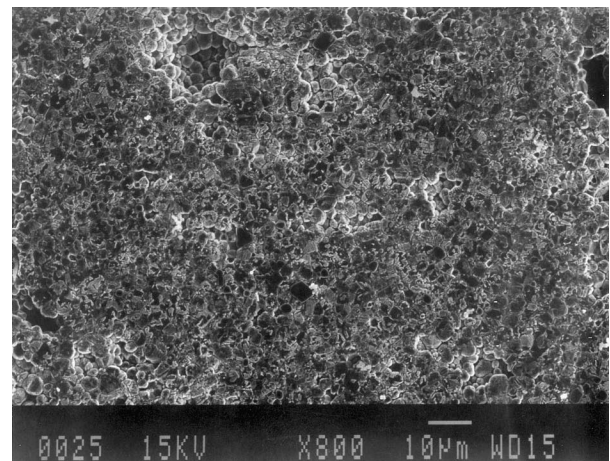
Fig. 3. Schematic diagram of the sintering system.

3.2. Dielectric behaviour

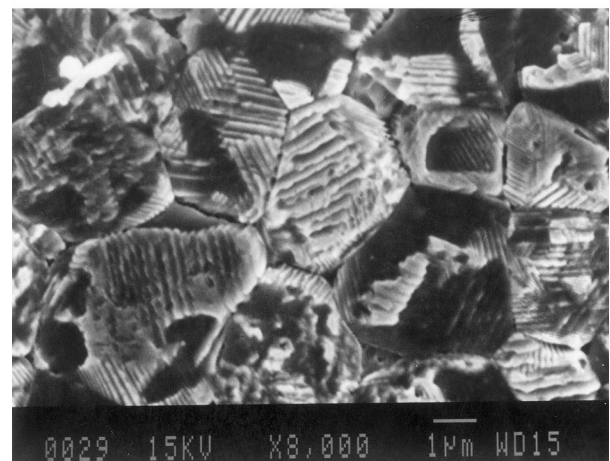
The samples used for dielectric measurements were plates of $5 \times 5 \times 1$ mm³. After polishing the electrodes are deposited by using air dried silver plates. Dielectric constant or relative permittivity, ϵ_r , and the dielectric loss factor, $\tan\delta$, were measured by using a HP impedance meter with a heating rate of about 1°C/min.

The dielectric loss is equal to $\tan\delta = \epsilon''/\epsilon'$, the relative permittivity ϵ_r is equal to $\epsilon_r = \epsilon' - j\epsilon''$, where ϵ' represents the dielectric constant and ϵ'' the relative loss factor.

Fig. 7 shows the variation of permittivity ϵ_r and dielectric loss $\tan\delta$ as a function of temperature for the frequencies of 1, 10, 50 and 100 kHz. The $\epsilon_r(T)$ curves show a peak situated at 347°C, similar to the internal friction peak P1 described in Section 3.3. This peak corresponds to the phase transition tetragonal-cubic (Curie temperature T_c) and its temperature does not change with frequency. This peak appears more clearly when the frequency is high, because at low frequency a



(a)



(b)

Fig. 4. Scanning electron micrograph of (a) compacted and sintered PHT and (b) polarization domains [after chemical etching with a HF (5%) solution].

significant background is present at high temperatures. The dielectric loss $\tan \delta(T)$ measured at various frequencies shows also a relaxation peak equivalent to the peak R1 observed by the mechanical loss peak (described in Section 3.3) and this peak is shifted as a function of frequency.

Table 2 gives the dielectric properties measured at 1 kHz at room temperature of the PHT ceramics elaborated by our coprecipitation method and also of a PHT elaborated by oxide mixing method.² In addition, we compare dielectric properties of others piezoelectric ceramics as doped and undoped PZT. This comparison allows us to show that the PHT ceramics present interesting dielectric properties as high ϵ_r and low dielectric losses.

3.3. Internal friction and elastic modulus

Internal friction $Q^{-1}(T)$ and Young's modulus $E(T)$ were measured from -180 to 450°C at a heating rate of $1^\circ\text{C}/\text{min}$ in vacuum by using samples driven in flexural

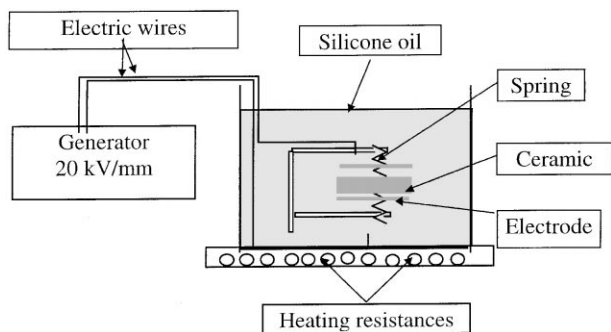


Fig. 5. Schematic diagram of polarization.

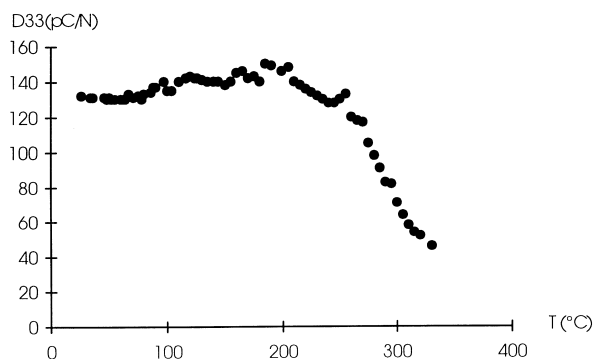


Fig. 6. Piezoelectric coefficient d_{33} as a function of temperature.

Table 1
Comparison of piezoelectric properties of PHT and PZT

Ceramics	d_{33} (pC/N)
PHT	140
PZT-500 ^(1,9)	140–250
Doped PZT ⁽¹⁾	160–550

vibration at resonance frequency.¹⁴ The frequency of vibration was about 2 kHz and the maximum strain amplitude was 10^{-6} .

Fig. 8 shows the variation in the elastic modulus E and the mechanical loss Q^{-1} as a function of temperature. The $E(T)$ curve shows two anomalies A2 (-80°C) and A1 (345°C) whereas the $Q^{-1}(T)$ curve shows a narrow peak P1 (345°C) and two broader peaks R2 (-120°C) and R1 (328°C).

The modulus anomaly A1 is associated with the P1 internal friction peak and corresponds to the phase transition tetragonal-cubic (T_c).

The composition of our ceramic $\text{PbHf}_{0.5}\text{Ti}_{0.5}\text{O}_3$ is near the morphotropic phase boundary determined by Jaffe et al.² where the two phases rhombohedral and tetragonal coexist. So the modulus anomaly A2 corresponds to the transition rhombohedral-tetragonal.

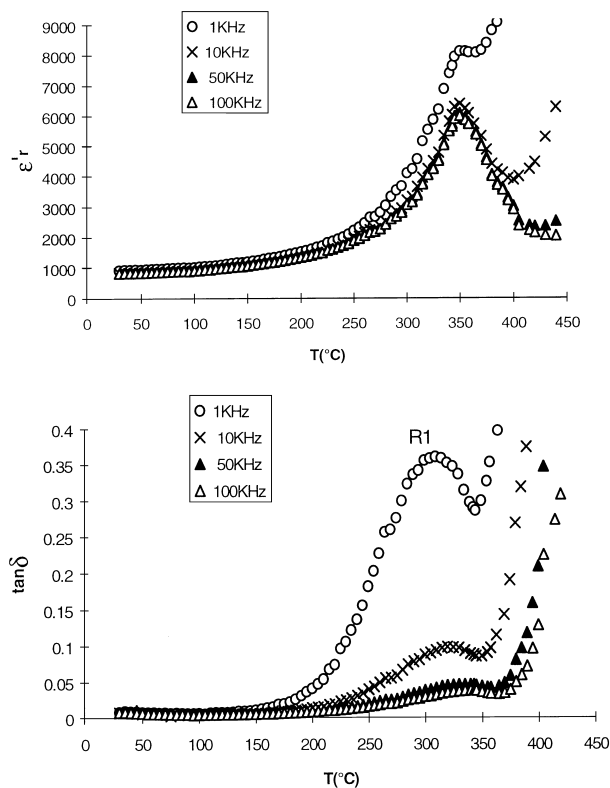


Fig. 7. Permittivity $\epsilon_r(T)$ and dielectric loss $\tan \delta(T)$ measured at 1, 10, 50 and 100 kHz.

Table 2
Dielectric properties of PHT and PZT ceramics measured at 25°C for 1 kHz

Ceramics	ϵ_r	$\tan \delta$
PHT	820	0.008
PHT ⁽²⁾	600	–
PZT ⁽³⁾	670	0.015
Doped PZT ⁽⁹⁾	1000–3500	–
$\text{PbCa}(\text{Ti}, \text{Zr})\text{FeO}_3$ ⁽¹³⁾	650	0.0015

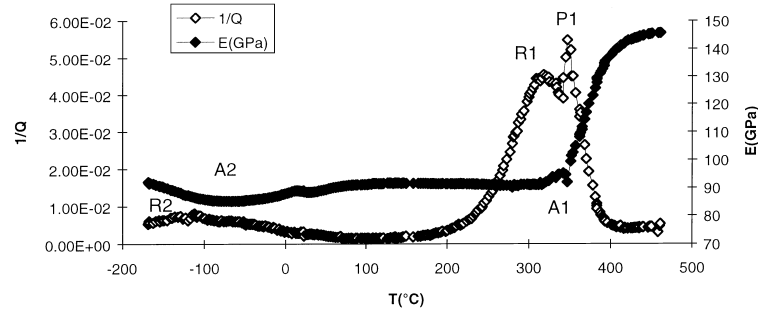


Fig. 8. Variation of internal friction Q^{-1} and Young's modulus E with temperature ($f = 2$ kHz).

Before the two anomalies A1 and A2, Q^{-1} peaks R1 and R2 appear, located in the temperature ranges that correspond to the tetragonal and rhombohedral structures respectively.

In order to specify the nature of the observed peaks and to determine their activation parameters, experiments at low frequency < 1 Hz by using an inverted pendulum were performed.¹⁵ The mechanical loss $Q^{-1}(T)$ were measured from 25 to 450°C at a heating rate of 1°C/min in vacuum.

The effect of frequency is shown in Fig. 9; with a frequency increase, the R1 peak temperature increases whereas the P1 peak (also associated with a modulus anomaly A1) appears at the same temperature, the P1 peak height decreasing with a frequency increase (it completely disappears for a frequency of 1 Hz).

3.4. Discussion

Anelastic and dielectric behaviour in ferro-electric ceramics has been studied by some authors^{9,16} who have shown that internal friction and dielectric loss of PZT and Ba TiO₃ are due to the motion of 90 and 180°C domains walls.¹³ These results have been confirmed recently by Cheng et al.¹⁵ and Bourim et al.¹⁷ The new results we have obtained on the PHT ceramics show a

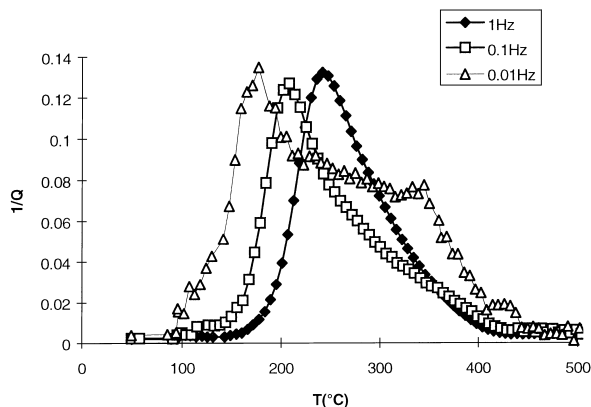


Fig. 9. Variation of Q^{-1} with temperature for different frequencies.

similar behaviour comparatively to the PZT ones. The internal friction and modulus curves show two anomalies which are due to the following phase transitions: tetragonal to cubic (T_c) and rhombohedral to tetragonal.

The permittivity curves shows equally the T_c temperature (Fig. 7).

Furthermore, internal friction and dielectric loss present two relaxation peaks R1 and R2 near about 300 and -100°C , respectively. Again, the PHT behaviour is very similar to the PZT one.¹⁷

These peaks can be described as relaxation processes. The peak temperature depends on the frequency according to the Arrhenius equation. The relaxation time can be written as:¹⁴

$$\tau = \tau_0 \exp(H/kT)$$

where T is the absolute temperature, k the Boltzmann constant, H the activation energy and τ_0 the pre-exponential factor.

For a Debye peak, the condition for the peak is $\omega\tau = 1$. This gives:

$$\ln(2\pi f) = -\ln(\tau_0) - H/kT_p$$

where T_p is the peak temperature, $\omega = 2\pi f$, f is the vibration frequency.

From the above results, the activation energy H and the relaxation time τ_0 of the R1 peak are determined by plotting $\ln f$ versus $(1/T_p)$ (Fig. 10). Taking into account the results obtained in the kHz and Hz ranges by internal friction or dielectric loss, the following values are found:

$$H = 1.53\text{eV} \quad \tau = 1.36 \cdot 10^{-16}\text{s}$$

These results are very similar to the ones obtained with a lead titanate zirconate PZT ceramic^{8,17} and also with barium titanate.¹⁵ These relaxation peaks observed in the ferroelectric phases are associated with the motion of domain walls and the interaction between the domain walls and the diffusion of oxygen vacancies in the

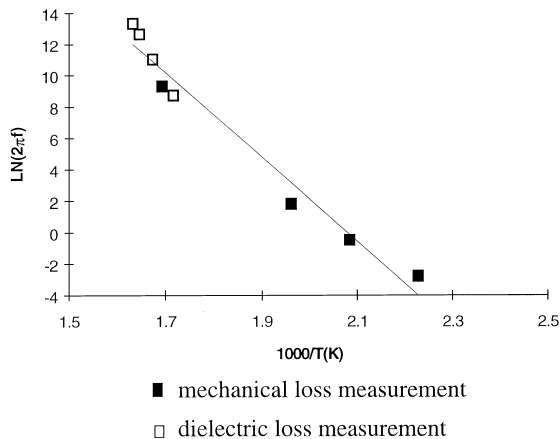


Fig. 10. Arrhenius plot of the R1 peak.

domains.^{15,16} Further experiments are necessary in order to confirm this hypothesis.

Concerning the dielectric and piezoelectric properties of PHT, the results presented in Tables 1 and 2 show that the PHT ceramics present interesting properties comparatively to the PZT ceramics: good permittivity, low dielectric loss and good piezoelectric coefficient.

These first results are encouraging and can be improved and optimized by acting on the PHT microstructures.

4. Conclusion

PHT powders can be prepared from pyrolysis of oxalic precursor and can be optimized for sintering.

The lead titanate hafnate $\text{Pb}(\text{Hf}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (PHT) ceramics show interesting dielectric and piezoelectric properties, comparatively to the lead titanate zirconate $\text{Pb}(\text{Zr}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (PZT) ceramics: good piezoelectric coefficient, good permittivity and low dielectric loss.

In the studied temperature range, measurements of elastic modulus, mechanical loss, dielectric loss and permittivity show the presence of two phase transitions (rhombohedral to tetragonal at -80°C and tetragonal-cubic at 345°C) and the motion of domain walls in the ferroelectric phase by the appearance of relaxation peaks for dielectric and mechanical losses.

The PHT ceramics behaviour is very similar to the PZT one.

It is clear that further investigations concerning processing and characterization of PHT are needed in order to improve the piezoelectric, dielectric and mechanical

behaviour of the PHT ceramics and to compare them more precisely with the PZT ones.

References

1. Uchino, K., Ferroelectric ceramics. In *Materials Science and Technology, Vol. 11, Structure and Properties of Ceramics*, ed. M. Swain. VCH, Weinheim, 1994, pp. 635–677.
2. Jaffe, B., Roth, R. S. and Marzullo, S., Properties of piezoelectric ceramics in the solid solution series lead titanate–lead zirconate–lead oxide: tin oxide and lead titanate–lead hafnate. *J. Res. Nat. Bur. Stds.*, 1955, **55**, 239–254.
3. Grange, G. Matériaux piézoélectriques à faible pression de transition ferro-antiferroélectrique utilisables en conversion d'énergie mécanoélectrique. Thèse Doct. Etat Sci., Lyon, 1984, No. IDE 8407.
4. Descamps, M., Tronc, P., Laurent, P. and Thierry, B., Elaboration de céramiques piézoélectriques de type PNZT par coulage en bande. *Silicates Ind.*, 1992, **5**, 163–171.
5. Villegas, M., Moure, C., Jurado, J. R. and Duran, P., Improvement of sintering and piezoelectric properties of soft lead zirconate titanate ceramics. *J. Mat. Sci.*, 1994, **29**, 4975–4983.
6. Yamamoto, T., Optimum preparation methods for piezoelectric and their evaluation. *Am. Ceram. Bull.*, 1992, **71**, 978–985.
7. Cheng, B. L., Gabbay, M., Duffy, W. and Fantozzi, G., Mechanical loss, Young's modulus associated with phase transition in barium titanate based ceramics. *J. Mat. Sci.*, 1996, **31**, 4951–4955.
8. Härdtl, K. H., Electrical and Mechanical Losses in Ferroelectric Ceramics. *Ceram. Int.*, 1982, **8**, 121–127.
9. Zhang, X. L., Chen, X. L., Cross, L. E. and Schulze, W. A., Dielectric and piezoelectric properties of modified lead titanate zirconate ceramics from 4.2 to 300 K. *J. Mat. Sci.*, 1983, **18**, 968–972.
10. Favotto, C., Satre, P., Sebaoun, A. and Roubin, M., Elaboration à partir de précurseurs oxaliques et caractérisation de poudres d'oxyde $\text{PbHf}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (PHT). *Ann. Chim. Sci. Mat.*, 1995, **20**, 281–292.
11. Lakhlifi, A., Satre, P., Sebaoun, A. and Roubin, M., Elaboration de poudres d'Oxyde de Hafnium stabilisé à partir de précurseurs oxaliques. *Ann. Chim. Fr.*, 1993, **18**, 565–572.
12. Ezahri, M., Etude de la solubilité dans l'eau et de la décomposition thermique des oxalates complexes. Thèse, Université de Lyon (France), 1994.
13. Arlt, G., Dederichs, H. and Herbiet, R., 90° -Domain wall relaxation in tetragonally distorted ferroelectric ceramics. *Ferroelectrics*, 1987, **74**, 37–53.
14. Nowick, A. S. and Berry, B. S., *Anelastic Relaxation in Crystalline Solids*. Academic press, New York, 1972 (Chapter 3).
15. Cheng, B. L., Gabbay, M. and Fantozzi, G., Anelastic relaxation associated with the motion of domain walls in barium titanate ceramics. *J. Mat. Sci.*, 1996, **31**, 4141–4147.
16. Potsnikov, V. S., Pavlov, V. S., Gridnev, S. A. and Turkov, S. K., Interaction between 90° domain walls and point defects of the crystal lattice in ferroelectric ceramics. *Soviet Physics-Solid State*, 1968, **10**, 1267–1270.
17. Bourim, E. M., Idrissi, M. H., Cheng, B., Gabbay, M. and Fantozzi, G., Elastic modulus and mechanical loss associated with phase transitions and domain walls motions in PZT based ceramics. *J. Phys.*, (1996) IV, **6**, C8-633–C8-6.