Temperature Dependent Electrical and Micromechanical Properties of Lanthanum Titanate with Additions of Yttria

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Introduction

Lanthanum titanate (La$_2$Ti$_2$O$_7$) a layered distorted perovskite (1) with space group Pna2$_1$ (Fig 1) has been shown to have potential as a high temperature piezoelectric (2). However this highly refractory oxide compound must be consolidated at relatively high temperatures ~ 1400 °C. Commercial La$_2$Ti$_2$O$_7$ powders were mechanically alloyed with additions of Y$_2$O$_3$ to lower the consolidation temperature by 300°C and to provide post processing mechanical stability. Temperature dependent electrical, elastic and anelastic behavior were selected as nondestructive means of evaluating the effects of yttria on the properties of this ferroceramic material.

Method and Materials

Lanthanum titanate powders were hot pressed at 1100°C into bars and from air sintered from aqueous based slurry tapes, for the mechanical and electrical measurements, respectively. Anelastic behavior as a function of temperature was determined by observation of the time dependent amplitude free decay of the sample. Temperature dependent elastic properties were determined by establishing continuous flexural vibrations in the material at its lowest resonance frequency at 3 kHz. Two terminal electronic characterizations were performed using a Solartron Analytical frequency response analyzer, model 1260 with the dielectric interface model 1296. Polarization measurements were performed with a Radiant Technologies Precision ferroelectric tester. Density and electron microscopy was performed on selected test samples. The partial density of states and band structure was calculated based upon energy minimization using density functional pseudo potentials. The computations were performed with Materials Studio's CASTEP atomic simulation software code. The calculations were run on a LINUX based operating system using dual Itanium 64 bit 1 GHz processors.

Results and Discussion

The results (Fig 2) of hot pressing lanthanum titanate with increasing amounts of yttria shows an increase in density as well as elastic modulus approaching the theoretical value of 5.78 g/cc and 181 GPa, respectively. Scanning electron micrographs (Fig 3) reveal numerous irregular and isolated pores, which are likely to prohibit full densification. However Fig.4 illustrates a typical microstructure with addition of yttria, only 0.1 mol % in this case. The light and dark grey regions are various phases of lanthanum titanate along with alumina inclusions (black), which were likely introduced in the milling process. To help determine the nature of the yttria/lanthanum titanate interface single
crystals were grown (Dr. Ali Sayir, NASA Glenn) and high resolution transmission microscopy was performed (Dr. Y.L. Chen, NASA Glenn). The HRTEM micrograph (Fig 5) reveals the yttria/lanthanum titanate interface with a coherent intermediate compound between them, most likely yttrium titanate.

Applying an external electric field to the samples at elevated temperatures reveals hysteresis like behavior (Fig. 6). Saturation occurs at 360°C and 1.4 kV/cm. Temperature dependent, low electric potential (E = 0.1 volt rms), complex impedance tests were performed on platinum/ferroelectric/platinum cells to determine the electronic losses. Figures 7 and 8 illustrate the real and imaginary impedance of lanthanum titanate at 600°C in air. The imaginary part of the complex impedance (Fig. 9) plotted as a function of frequency and temperature reveals a thermally activated peak, which decreases in magnitude as the temperature increases. This is consistent with a mechanism whereby the crystal lattice expands reducing the reorientation energy of electro-elastic defects. The calculated band structure and partial density of states (Fig. 10) gives insight into the electronic mechanisms of this insulating ferroelectric and possible doping scheme to alter its electronic properties (3). A direct 2 eV band gap is predicted in the G symmetry direction in the Brillouin zone. The valence band is made of hybridized titanium 3d and oxygen 2p orbitals while the conduction band consists of a p + d hybrid orbital made largely from the lanthanum 5d and titanium 3d atomic orbitals. Smaller contributions to the valence band come from the lanthanum 5p and oxygen 2p levels. Hence for this A₂B₂O₇ compound, the A site is best suited to host single valence cation substitutions, while multi-valence substitutions would best occur at the B site.

One order of magnitude reduction in yttria content results in a reduction in elastic modulus (Fig. 11) below 5 mol% yttria differences in both the stiffness and in the elastic temperature coefficient are not substantial, while still producing excellent mechanical properties at elevated temperatures. One mechanical loss peak (Fig 12) appears at 466°C approximating a single Debye peak. The peak of the relaxation occurs at 3 kHz; nearly identical in frequency and temperature to the electrical relaxation noted in Figs. 6 and 7. As the amount of yttria increases the internal friction peak also increases. Based upon the magnitude, temperature and frequency of this peak, point defects are the likely mechanism. Hence by controlling the concentration of yttria we are able to tailor the population of defect clusters which may influence the domain mechanics of this material. Both the anelastic and elastic temperature spectrum provides additional evidence of minimal residual glassy phases at the grain boundaries.
Summary of Findings

- Additions of yttria do not degrade the electromechanical properties of lanthanum titanate.
- Y₂O₃/La₂Ti₂O₇ exhibits extremely low internal friction and hence has mechanical fatigue resistant properties at low strains.
- Micromechanical observations manifested themselves in the electrical nature of these materials.
- Both the electrical and mechanical relaxations appear to be thermally activated processes.

References:


Fig. 1 Lanthanum titanate with crystal structure Pna2₁, a = 25.745 Å,
b = 7.18 Å, c = 5.547 Å, where the gray octahedral denote the titanium
surrounded by oxygen (red) anions and lanthanum cations (blue).
Single Crystal La$_2$Ti$_2$O$_7$
Density = 5.79 g/cm$^3$
Elastic Modulus = 181 GPa
Kimura, et al 1972

Fig. 2 Effect of yttria content on the elastic modulus and density of lanthanum titanate
Fig. 3 Scanning electron micrograph of hot pressed lanthanum titanate with no yttria showing various phases and isolated irregular pores.
Fig. 4 Electron micrograph of lanthanum titanate with 0.1 mol % yttria with minimal porosity.
Fig. 5 High resolution electron transmission micrograph of a lanthanum titanate / yttria interface with the intermediate YTiO$_3$ phase.
Fig. 6 Hysteresis of $\text{Li}_2\text{O}_7$ with 0.1 mol% $\text{Y}_2\text{O}_3$ at 360°C in air.
Fig. 7 Real part of the impedance of La$_2$Ti$_2$O$_7$ with 0.1 mol % yttria at 600°C.
Fig. 8  Imaginary part of the impedance of La$_2$Ti$_2$O$_7$ with 0.1 mol % yttria at 600°C.
Fig.9 Temperature and frequency dependent AC impedance of 
La$_2$Ti$_2$O$_7$ with 0.1mol% Y$_2$O$_3$. 
Fig. 10 Calculated band structure and partial density of states for \( \text{La}_2\text{Ti}_2\text{O}_7 \).
Fig. 11 Temperature dependent modulus of lanthanum titanate/yttria alloys.
Fig. 12 Temperature and Y$_2$O$_3$ dependent anelastic behavior of La$_2$Ti$_2$O$_7$. 