



EFFECT OF CALCIUM ON THE PIEZOELECTRIC AND DIELECTRIC CHARACTERISTICS OF CERAMICS MADE FROM Sm-MODIFIED PbTiO₃

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Article History: Received: 12.06.2023

Revised: 14.07.2023

Accepted: 31.07.2023

Abstract

This study looked at how calcium dopants affected the piezoelectric and dielectric characteristics of ceramics made from lead titanate (PbTiO₃) that had undergone Sm modification. By using traditional mixed-oxide techniques and sintering at 1200^oC, Sm-modified PbTiO₃ ceramics with a composition of (Pb_{0.88x}Ca_xSm_{0.08}) (Ti_{0.98}Mn_{0.02})O₃ were created. We were able to demonstrate that adding Ca to PbTiO₃-based ceramics allows for substantially larger thickness electromechanical coupling coefficients (> 0:57) while maintaining tiny planar electromechanical coupling coefficients (kp). These doped ceramics have undergone microstructural and compositional studies utilizing an X-ray diffractometer (XRD) and scanning electron microscope (SEM).

Keywords: SEM, Ceramic, XRD, Lead titanate.

Introduction

Due to their low dielectric constant of about 200 and high Curie temperature (T_c) of 490^oC, lead titanate (PbTiO₃) ceramics have gained attention recently and are preferred over PZT ceramic systems for high-temperature and high-frequency transducer applications. However, due to their significant structural anisotropy (c/ a 1:064), pure lead titanate ceramics are very difficult to sinter. The significant anisotropy of ceramic material weakens with T_c cooling. Additionally, the ceramics

with low resistivity (107–108 cm) are difficult to pole.

The lattice anisotropy is decreased [3–7] and the samples grow denser by substituting isovalent (Ca₂; Ba; Cd; etc.) or off-valent (Sm; Gd; Y; etc.) ions into the Pb₂ sites. These modified PbTiO₃ ceramics will have a tiny planar electromechanical coefficient (kp) and a moderately high thickness electromechanical coupling coefficient (kt). In other words, the thickness vibration kt will have a significantly bigger electromechanical coupling factor than the planar extensional

vibration. In comparison to PZT ceramics, PbTiO₃ exhibits a greater kt/kp ratio with the addition of Ca or Sm. Due to this characteristic, PbTiO₃-based ceramics are suitable for high-frequency uses, including piezoelectric transformers and SAW devices.

(Pb_{0.85}Sm_{0.1})(Ti_{0.98}Mn_{0.02})O₃ ceramics exhibit very high electromechanical anisotropy, according to a number of studies [10–12]. To study the dielectric and piezoelectric characteristics, we create the (Pb_{0.88x}Ca_xSm_{0.08})(Ti_{0.98}Mn_{0.02})O₃ (x 0:110.17) system in this research.

Experimental procedure:

The sample was prepared using a traditional ceramics preparation method. Pure reagent

powders (>99.0% purity) PbO, TiO₂, Sm₂O₃, MnO₂, and CaCO₃ were used to combine the raw ingredients. The materials (Pb_{0.88x}Ca_xSm_{0.02})(Ti_{0.98}Mn_{0.02})O₃, x 0:110.17, were created by calcining at 900°C for 2 hours while adding extra PbO to prevent PbO from volatilizing throughout the firing process. The powders were then dried and ground with 8% of a 5% PVA solution after that. The samples were then put under pressure of 25 kg cm² to form a disk with a diameter of 12 mm and a thickness of 1.5 mm. The specimen was then sintered isothermally at 1200°C for 2 hours at a heating rate of 10°C min⁻¹. PbTiO₃ powder was used to maintain a PbO-rich environment in order to reduce the lead during sintering loss. Figure 1 depicts the flow diagram of the sample preparation process.

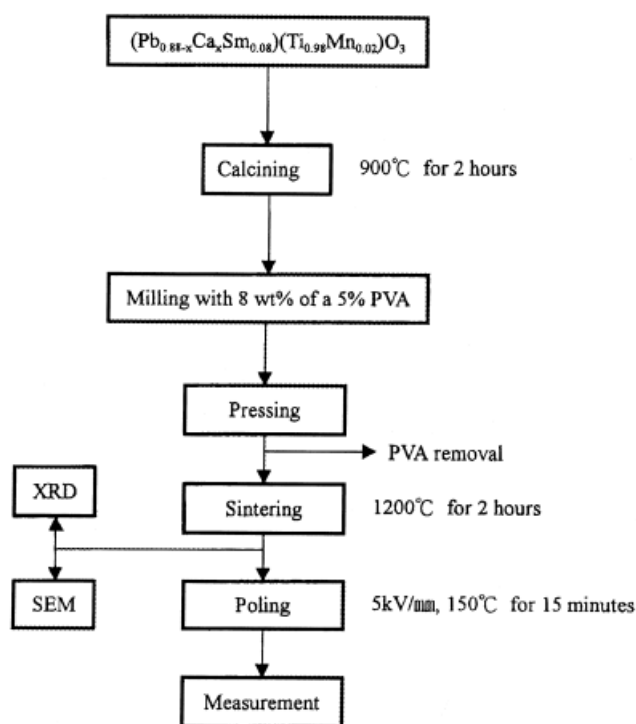


Figure 1: Flow diagram of the sample preparation procedure.

The Archimedes technique was used to calculate the bulk densities of sintered substances. On both sides of the sample, silver paste was applied to create electrodes in order to analyze the electrical

characteristics. The sample was then fired for 20 minutes at 800°C. After poling under 5 kV mm⁻¹ bias at 150°C in a silicone oil bath for 15 min, the dielectric (measured at 1 kHz) and piezoelectric characteristics

were assessed using an impedance analyzer (HP4194A). The resonance measuring

technique was used to determine the piezoelectric characteristics.

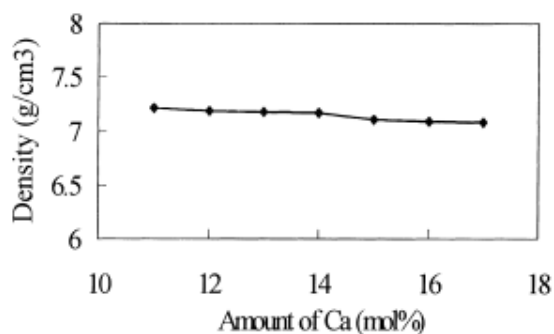


Figure 2. Dependence of the bulk density on the amount of Ca additives.

Utilizing an X-ray diffractometer (XRD) to identify the phase relations for the sintered body and a scanning electron microscope (SEM) to see the microstructures.

Results and discussion

The bulk density is shown in Figure. 2 as a function of the Ca ceramic content. With more Ca replacements, the density fell a little. Ca is lighter than Pb, therefore this finding makes sense. All of the samples were >95% theoretically dense after sintering, which is required to withstand the

strong electric field (50 kV cm⁻¹) in PbTiO₃-based systems. In Fig. 3, XRD patterns of ceramics (Pb_{0.88x}Ca_xSm_{0.08}-Ti_{0.98}Mn_{0.02})O₃ are shown. PbTiO₃ and Ca-doped PbTiO₃ ceramics both exhibit large peaks at (1 0 1), and they are all tetragonal in structure. PbTiO₃ and Ca-doped PbTiO₃ samples' XRD patterns don't seem to vary much. As Ca dopants rise, the peak values of (0 0 2) and (2 0 0) (about 458) migrate toward one another. when a result, when the quantity of Ca additive was increased, the lattice anisotropy, or c/a ratio, reduced, as seen in Figure 4.

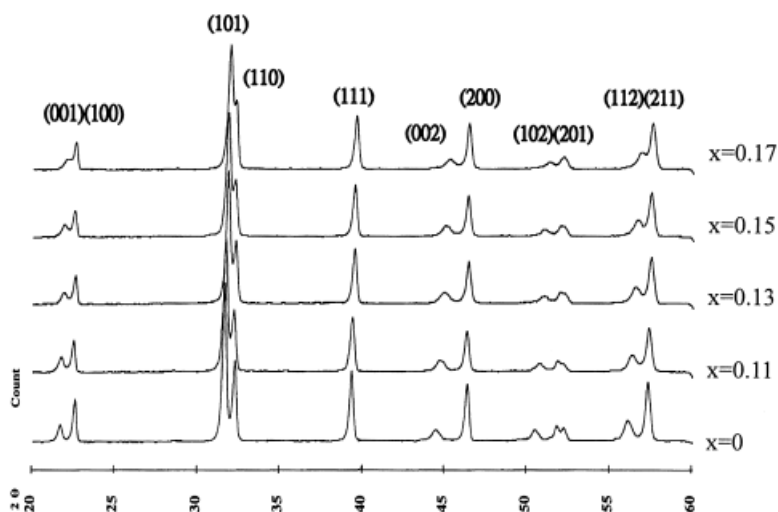


Figure 3. XRD patterns of (Pb_{0.88x}Ca_xSm_{0.02}) (- Ti_{0.98}Mn_{0.02})O₃ samples.

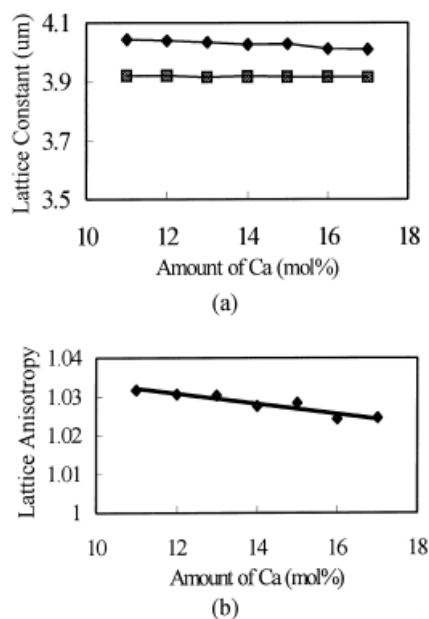


Figure 4. Dependence of the (a) lattice constant and (b) lattice anisotropy on the amount of Ca additives.

Ca²⁺ concentration increases cause the microstructure of the PbTiO₃ system to transform into a somewhat cubic shape because CaTiO₃ is cubic in phase at room temperature.

Both the PbTiO₃ and Ca-doped PbTiO₃ samples have homogeneous microstructures and are very dense, as evidenced by the SEM pattern in Fig. 5. Grain sizes of 1.5–2 μm, which are smaller than those found in earlier research [14]. The dependency of particle size on the Ca

dopant is seen in Fig. 6. It was discovered that Ca dopant hardly altered grain size.

The samples' dielectric constant and loss factor are shown in Fig. 7(a) and (b), respectively, along with the concentration of Ca. Because the T_c of the PbTiO₃ system falls as the concentration of Ca₂ grows but the loss factor hardly changes, it demonstrates that the dielectric constant increases proportionally with the increase in the quantity of Ca at ambient temperature.

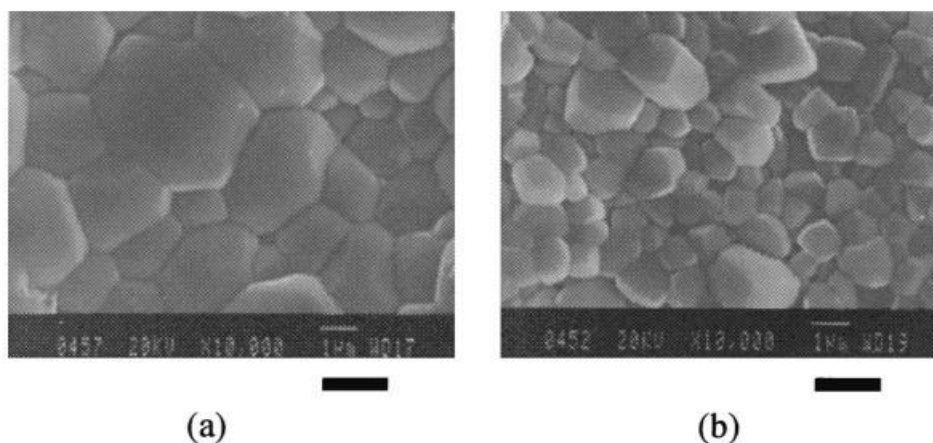


Fig. 5. SEM photographs of (a) (Pb_{0.85} Sm_{0.1})(Ti_{0.98} Mn_{0.02})O₃ and (b) (Pb_{0.75}Ca_{0.13} Sm_{0.08})(Ti_{0.98}Mn_{0.02})O₃ samples sintered at 1200°C for 2 h (bar 2 μm)

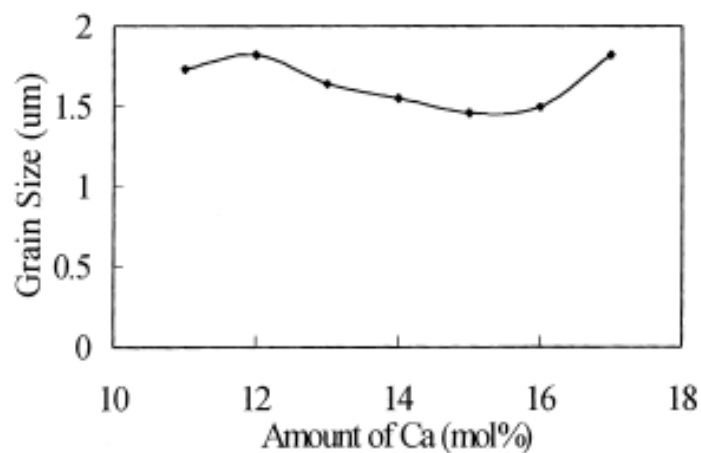


Figure 6. Dependence of the grain size on the amount of Ca additives.

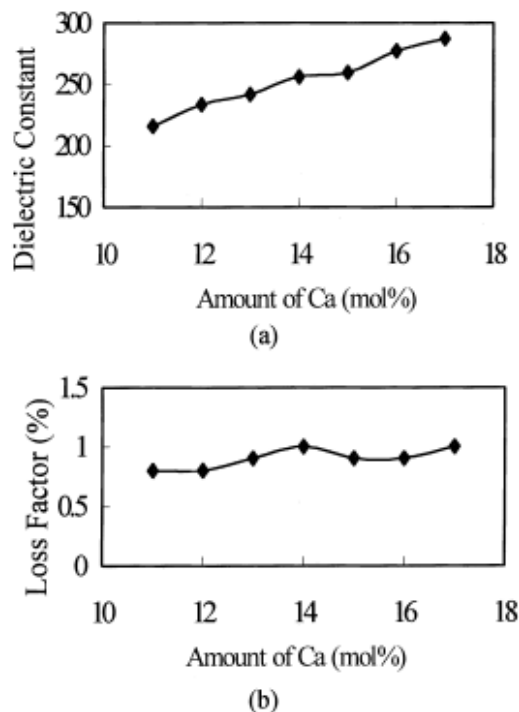


Figure 7. Dependence of the (a) dielectric constant and (b) loss factor on the amount of Ca additives.

For Ca dopant concentrations of 11% and 17%, the dielectric constant is 210 and 290, respectively. For all components, the dielectric loss was less than 1%. The

samples' dielectric constants were doped with Ca and Sm are higher than samples that doped with Ca or Sm, respectively.

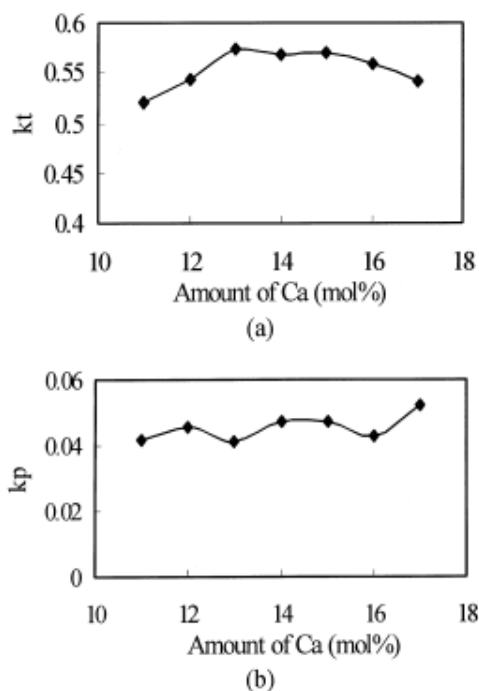


Fig. 8. Dependence of the (a) thickness coupling factor and (b) planar coupling on the amount of Ca additives.

Figure 8 displayed the outcomes of the coupling factors for thickness (kt) and planarity (kp). Kp rises first as Ca additive increases and reaches its maximum value of 0.574 as Ca 13 mol%. It is clear that the kp value for x 0:130.15 is around 0.57, which is greater than the values previously reported for lead titanate with a Sm modification [14]. The smallest value of kp occurs when Ca is less than 13 mol%, and the value ranges from 0.04 to 0.05 as Ca varies. When Figs. 4 and 7 were compared, we discovered that Ca dopants linearly enhance dielectric constant while decreasing lattice anisotropy. On the other

hand, when comparing Figs. 4 and 8, we discovered that the largest value of kt/kp occurs at Ca 13 mol%, when neither the maximum nor lowest value of c/a was reached. Lattice anisotropy (c/a value) is thus unaffected by strong electromechanical anisotropy (kt/kp) in ceramics based on PbTiO₃. We believe that the concentration of doping is the main factor influencing kt . In our analysis, we find minimal correlation between grain size and kt . It most likely is because there was little variation in the grain size of our samples.

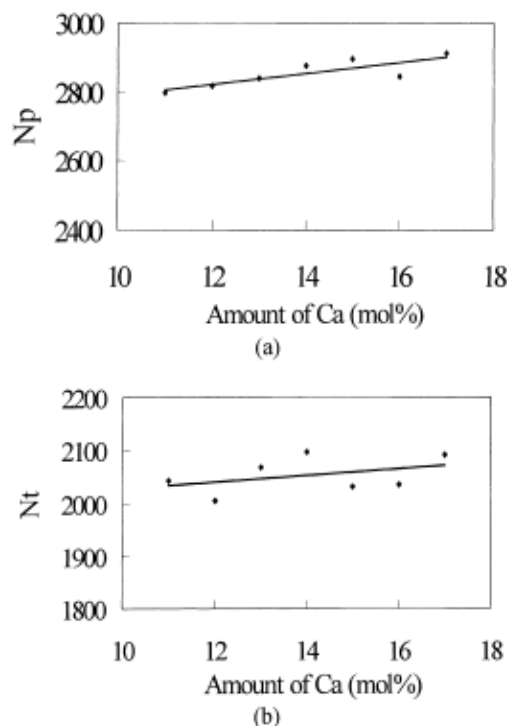


Figure 9. Frequency constant is shown against Ca quantity

There are about 2850 and 2050 kHz mm in the planar and thickness frequency constants, respectively.

Conclusion:

Simultaneous Ca and Sm additions maintain the excellent dielectric and anisotropy characteristics of the Sm- or Ca-modified PbTiO₃ ceramics while simultaneously reducing the lattice anisotropy (*c/a*). The T_c generally declined with increasing Ca doping level, ranging from 300°C for Ca 0:11% to 250°C for Ca 0:17% [15]. The Ca content ratio with the greatest *kt/k_p* value, which is Ca 0:13%, is what we consider to be the ideal Ca content ratio. It is possible to utilize the observed coupling coefficient, *kt*, of 0.57 as Ca 13–15 mol% in high-temperature and high-frequency applications.

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