Preparation and electrical properties of Pb(Yb_{0.5}Nb_{0.5})O_3 - PbHfO_3 - PbTiO_3 ceramics

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Abstract. This topic selects the ternary system Pb(Yb_{0.5}Nb_{0.5})O_3-PbHfO_3-PbTiO_3 ceramics for research. The preliminary phase diagram analysis of the ternary system can preliminarily determine the morphotropic phase boundary (MPB) of the ceramic system. This article also characterizes the electrical properties of the samples, tests their dielectric temperature spectra, determines the Curie temperature and its components, and further determines the phase boundary based on the ferroelectric properties. The samples are polarized under appropriate conditions and the piezoelectric coefficient d_{33} is tested. Finally, determine the best preparation process to analyze the properties of samples prepared under different conditions, and obtain high-quality ceramic samples.

1. Introduction

With the development of science and technology, due to the shortcomings of single-layer lead-based piezoelectric ceramic drivers such as high driving voltage and small displacement, it has been unable to meet the current needs of chip-type, integrated, and high-performance mechanical and electronic components. The multilayer lead-based piezoelectric ceramic actuator has the advantages of small size and large displacement, and has a wide range of applications in the field of precision driving. Ferroelectric ceramic materials have good dielectric and piezoelectric properties, especially ceramic materials with a high Curie temperature, which are widely used in many fields and have always attracted attention and a lot of research has been carried out. The binary system piezoelectric ceramic material Pb(Yb_{0.5}Nb_{0.5})O_3-PbTiO_3 has a higher distance temperature (T_C is 350-400°C), and its piezoelectric coefficient is also larger, the maximum can reach 500 pC/N, because of its relatively high Curie point, it can also guarantee good piezoelectric performance under high temperature conditions. PbZrO_3-PbTiO_3 and Pb(Yb_{0.5}Nb_{0.5})O_3 are combined into a new solid solution system Pb(Yb_{0.5}Nb_{0.5})O_3-PbZrO_3-PbTiO_3 has also been reported and studied. The obtained ceramic material has good performance at the phase boundary, the Curie temperature reaches 375°C, and the piezoelectric coefficient also reaches 600 pC/N. Although the quality of Hf^{4+} ion and Zr^{4+} ion are quite different, the ion radius of the two is not much different, and the ion polarizability is similar. So far, the research on PYN-PT ceramics is relatively mature, and the ceramic system has a high Curie Temperature (360°C), but the phase boundary of the binary ceramic system is narrow. This topic selects the new ternary system Pb(Yb_{0.5}Nb_{0.5})O_3-PbHfO_3-PbTiO_3 to study, determine the phase
boundary, and expect to obtain electrical properties. A better ceramic material has a higher Curie temperature, so this will be a new material with practical significance.\textsuperscript{[2]}

2. Materials and Methods

The ceramic material is synthesized according to the formula Pb(Yb\textsubscript{0.5} Nb\textsubscript{0.5})O\textsubscript{3}-PbZrO\textsubscript{3}-PbTiO\textsubscript{3} by solid-phase reaction method. The raw materials used are Pb\textsubscript{3}O\textsubscript{4}(99.9%), TiO\textsubscript{2}(99.9%), Nb\textsubscript{2}O\textsubscript{5}(99.9%), HfO\textsubscript{2}(99.99%) and Yb\textsubscript{2}O\textsubscript{3}(99.9%). The perovskite synthesis adopts the Wolframite Precursor Method (Wolframite Precursor Method) invented by RT Shrout and others in recent years. First, Yb\textsubscript{2}O\textsubscript{3} and Nb\textsubscript{2}O\textsubscript{5} are matched in a ratio of 1:1, and they are ground in a DL-1 planetary ball mill for 8 hours. (The grinding ball and the grinding pot are all agate, and the grinding medium is absolute ethanol). After drying, the mixture is calcined at about 850°C for 2h to avoid the formation of pyrochlore phase.

X-ray diffraction results show that the calcined powder is single-phase wolframite (YbNbO\textsubscript{4}), and then Yb\textsubscript{2}O\textsubscript{3}, Nb\textsubscript{2}O\textsubscript{5}, Pb\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2} and HfO\textsubscript{2} are pressed as (1-x)Pb(Hf\textsubscript{1-y}Ti\textsubscript{y})O\textsubscript{3}-xPb(Yb\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3} stoichiometric ratio ingredients, after 12 hours of grinding according to the above grinding conditions, 1150°C ~1250°C (different formulations have different synthesis temperatures) 2 hours of calcination synthesis. The powder synthesized by the precursor method is easy to crush, and only needs a short time of ball milling to reach the sub-micron level. In order to compensate for the volatilization of lead oxide during the synthesis and sintering process, 0.5% (mass ratio) of excessive lead oxide was added during the batching. The powder synthesized by calcination is a single-phase perovskite. The synthesized powder is ground under the above-mentioned grinding conditions for 8 hours, and after drying, it is pressed into a disc with a diameter of 14mm × 1mm by adding a polyvinyl alcohol binder. Set aside after plastic ejection.

There is a close relationship between the performance of the material and the structure. The piezoelectric and dielectric properties of piezoelectric ceramics are determined by the crystal structure of the material. The phase diagram (refers to the phase diagram at room temperature) can clearly and intuitively reflect the material. The basic phase composition of different components. For a ternary piezoelectric ceramic material, if its phase diagram is known, during application development, you can select the appropriate area on the phase diagram for targeted material development.\textsuperscript{[3]} Draw the phase diagram of Pb(Y\textsubscript{0.5}Nb\textsubscript{0.5})O\textsubscript{3}-PbTiO\textsubscript{3}-PbHfO\textsubscript{3}(PYN-PT-PH) ternary system ferroelectric ceramic materials in order to have an overall understanding of the piezoelectric and dielectric properties of the series of materials. In-depth experimental research has been carried out on the material composition of certain areas on the phase diagram. The decomposition, compound reaction point and pre-sintering temperature range of Yb\textsubscript{2}O\textsubscript{3}, Nb\textsubscript{2}O\textsubscript{5}, Pb\textsubscript{3}O\textsubscript{4}, TiO\textsubscript{2} and HfO\textsubscript{2} powder mixture were judged by thermogravimetry-differential thermal analysis.

Pre-firing and sintering are processes that cause chemical reactions between raw materials. During the pre-sintering process, the oxides in the raw materials undergo thermochemical reactions to form the required solid solution. At the same time, the sample can also be used to remove some impurities during the pre-sintering process, so that the ceramic sample becomes more dense and avoids holes and cracks in the subsequent sintering process. In addition, pre-firing can also increase the mechanical toughness of ceramics. Ceramic sintering is a general term for the densification process that increases the mechanical properties of ceramic samples, reduces the surface area of the embryo body, and reduces the porosity under high temperature and other conditions. Sintering refers to the physical and chemical reaction and densification of the green body through a certain high temperature treatment to form the required microstructure. The driving force of sintering is the reduction of the surface energy of the molecules and the free energy of the system. In this experiment, the pre-sintering temperature and sintering temperature time were used to explore the effects of reaction sintering (1-x)PYN-xPHT ceramics on the structure and piezoelectric dielectric properties.\textsuperscript{[4]}
3. Results & Discussion

3.1. Thermal weight loss of powder-differential thermal analysis
Figure 1. TG-DTA curve of mixed powder shows the thermal weight loss-differential thermal analysis (TG-DTA) curve of a mixture of Yb$_2$O$_3$, Nb$_2$O$_5$, Pb$_3$O$_4$, TiO$_2$ and HfO$_2$ powders configured in a stoichiometric ratio. It can be seen from the figure that there is an obvious exothermic peak near 580°C, which may be caused by the combustion exotherm caused by mixing organic matter; there is an endothermic peak near 800°C, indicating that there is a substance in the vicinity of this temperature. Decomposition reaction; a continuous exotherm began to appear at 820°C, indicating that the synthesis reaction has begun. According to this analysis, the pre-burning temperature can be roughly selected in the range of 825°C to 850°C.

3.2. Research on piezoelectric ceramic phase diagram
Based on the research of binary system ceramics, the preliminary phase diagram analysis of the studied ternary system is carried out first. Figure 2 shows the morphotropic phase boundary of ceramic sample is in the coexistence of the three sides and the tetragonal phase, and it is close to the tetragonal phase. It can be known from the literature that the morphotropic phase boundary of the binary system ceramic PbHfO$_{3-x}$PbTiO$_3$ is at x=0.50, and the morphotropic phase boundary of PYN-xPT is at x =0.495, according to the phase boundary of the two, near the junction of the tripartite phase and the tetragonal phase, and close to the tetragonal phase, select some different components for the preparation of ceramic samples. It is observed that with the increase of PYN content, the (200)/(002) peaks gradually merge into one peak, indicating the phase change from the tetragonal phase to the rhombohedral phase. Based on this, the composition (1-x) PHT(40/60)-xPYN, where x = 0.17~0.21 is recognized as the MPB area. Figure 3 shows using the same method, the MPB area is used for other compositions (1-x)PHT(45/55)-xPYN is x = 0.10~0.13. Based on these XRD results, the MPB region and phase diagram of the PYN-PHT ternary system were confirmed.
3.3. The influence of pre-sintering temperature and sintering temperature on the phase structure and microstructure of 0.8Pb(Hf_{0.4}Ti_{0.6})O_3 - 0.2Pb(Yb_{0.5}Nb_{0.5})O_3 ceramics

Figure 4 shows the XRD patterns of ceramics prepared by different pre-firing temperatures. When the pre-sintering temperature is 850°C, the main crystalline phase of the perovskite type is formed, and as the pre-sintering temperature increases, the degree of crystallization becomes higher and higher. Ceramics are all perovskite structures in which three and tetragonal phases coexist. With the increase of the pre-burning temperature, the diffraction peaks gradually strengthened. In the solid phase reaction, when the pre-sintering temperature is 800°C, due to the low temperature, the pre-reaction of the raw materials is not sufficient, and the degree of powder crystallization is low, so that the time for real grain growth during sintering is reduced, so the grain growth Incomplete, insufficient removal of pores; when the temperature is high (such as 900°C), the raw material reacts completely, but the sintering phenomenon occurs due to excessive crystallization, which reduces the sintering activity of the powder and is not conducive to the growth of crystal grains; At a moderate temperature (such as 850°C), the reaction is sufficient, and the powder has a high degree of crystallization without excessive crystallization. At this time, the surface activity is high, and the sintering is conducive to the growth of ceramic grains and the formation of compact ceramics.

Sintering is a key process in the ceramic preparation process. The sintering temperature is generally selected at 1/2 - 3/4 of the melting point of the raw material. The specific sintering temperature needs to be explored according to the literature reports and the actual conditions of the laboratory, Sintering the same composition 0.8Pb(Hf_{0.4}Ti_{0.6})O_3 - 0.2Pb(Yb_{0.5}Nb_{0.5})O_3 at 1150°C, 1200°C, 1250°C three different temperatures.

The preparation of high-purity PYN-PHT ceramics with a perovskite phase structure requires a high sintering temperature. Because the sintering temperature is too high, it will cause the volatilization of lead oxide PbO, which will cause environmental pollution and the uncertainty of the composition ratio will greatly reduce the performance of PYN-PHT ceramics. Therefore, ensuring the high-voltage electrical characteristics of PYN-PHT ceramics at lower sintering temperatures is one of the key scientific issues in this research. XRD tests were performed on ceramic samples sintered at different temperatures.

Figure 5 shows the XRD patterns of three ceramic samples sintered at different temperatures. It can be seen from the figure that the samples can become good perovskite phases at three temperatures. At the three sintering temperatures, impurity phases appear around 30 degrees, and the impurity phases become more and more obvious as the temperature rises. This is the impurity phase that exists in all niobates. Some literature believes that it is PbO. Some think it is pyrochlore phase, without a clear understanding.
3.4. The influence of pre-sintering temperature and sintering temperature on the piezoelectric and dielectric properties of 0.8Pb(Hf0.4Ti0.6)O3 -0.2Pb(Yb0.5Nb0.5)O3

Pre-sintering can synthesize the perovskite-type phase structure in advance, increase the speed of ceramic firing, reduce shrinkage and porosity, and avoid sample cracking. Figure 6 shows the comparison of piezoelectric dielectric properties of ceramic samples pre-fired at different temperatures. After the polarized ceramic sample, test the piezoelectric coefficient d33, it can be seen from the figure that when the pre-sintering temperature is lower than 850°C, d33 increases rapidly with the increase of temperature; when the pre-sintering temperature rises to 850°C, d33 is Maximum value; when the pre-burning temperature is increased, d33 decreases rapidly. The piezoelectric and dielectric properties of ceramic d33 increased first and then decreased with the increase of the pre-sintering temperature. The ceramic sample has the largest grain size and compact structure at 850°C. As the grain size increases, the ratio of the grain boundary to the total volume decreases. During the polarization process, the clamping stress generated at the grain boundary is low, the internal friction is small, the electrical domain is easy to turn, and the material is easy to be polarized. Figure 7 and Figure 8 shows the ceramic structure is compact, which is beneficial to improve the performance of the material, that is, d33, εr reach the maximum, and tanδ is relatively small, so the pre-sintering temperature can be set at 850°C and the pre-sintering time is 2h. The piezoelectric coefficient of the ceramic samples sintered at 1200°C is significantly higher, showing strong piezoelectric properties. It is just because there are more pores under the condition of low temperature, the density is not up to the requirement, and the performance is not good. If the temperature is too high, too much liquid phase will appear and adhesion will occur. At the same time, the volatilization of lead will cause serious degradation of sample performance. Through the test and analysis of the micro morphology, phase formation and electrical properties at different sintering temperatures, it is found that the phase formation and micro morphology of the ceramic samples sintered at a temperature of 1200°C are better than those of the other two temperatures. The electrical properties are It is also more advantageous, so the sintering temperature can be set at 1200°C and the sintering time is 2h.
4. Conclusions
This thesis studies the Pb(Yb0.5Nb0.5)O3-PbHfO3-PbTiO3 piezoelectric ceramic system, studies its preparation process, structural characteristics, electrical properties, etc. And finally obtains the following conclusions. First, prepare ceramic samples of different components, characterize their microstructure and phase, determine that the prepared ceramic samples have a dense structure, and analyze the XRD test results to initially determine the morphotropic phase boundary, which will provide for the smooth progress of the next experiment Conditions. Then the pre-sintering temperature and the sintering temperature are determined, the ceramic samples prepared at different temperatures are compared, and the X-ray diffraction and electrical properties are tested and analyzed. Through various performance tests of the ceramic samples of the system, it is found that the ceramic samples of the system have a higher Curie temperature, and the maximum Curie temperature is 348°C, which provides the possibility for its practical application; there is the largest piezoelectric coefficient at the boundary component, the largest piezoelectric coefficient d33 is 236 pC/N, and the dielectric loss is 4.8%, showing very good ferroelectric and piezoelectric properties. In summary, in the process of preparing Pb(Yb0.5Nb0.5)O3-PbHfO3-PbTiO3 piezoelectric ceramics by solid-phase reaction method, the pre-sintering temperature is very important to obtain high-quality ceramics. The pre-sintering temperature is appropriate, the sintering temperature range is wide, the grain size is moderate, the ceramic has high density and good performance. The best pre-sintering condition is 850°C, and the holding time is 2h. Under these conditions, the sintering temperature is 1200°C and the holding time is 2h. The obtained ceramic material has excellent piezoelectric dielectric properties. The ceramic prepared under this process condition with excellent performance and good repeatability, it has shown practical prospects in high-temperature piezoelectric ceramic sensors and transducers.
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References

[1] S.T.F. LeeK, H. Lam, X.M. Zhang, H.L.W. (2011) ChanHigh-frequency ultrasonic transducer based on lead-free BSZT piezoceramics[J]. Ultrasonics, 51 (7): 811-814.

[2] B. Jaffe, R. S. Roth, and S. Marzullo, (1995) “Properties of Piezoelectric Ceramics in the Solid Solution Series Lead Titanate-Lead Zirconate-Lead Oxide: Tin Oxide and Lead Titanate-Lead Hafnate,” J. Res. Natl. Bureau Stand, 55, 239–54.

[3] Morozovska AN, Eliseev E A, Glinchuk M D. (2007) Size Effects and Depolarization Field Influence on the Phase Diagrams of Cylindrical Ferroelectric Nanoparticles[J]. Physica B: Condensed Matter, 387 (1-2): 358-366.

[4] Dragan Damjanovic. (1998) Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics [J]. Rep. Prog. Phys, (61): 1267-1324.

[5] Jong Bong Lim, Shujun Zhang, Thomas R. Shrout. (2012) Modified Pb(Yb, Nb)O₃-PbZrO₃-PbTiO₃ ternary system for high temperature applications[J]. Ceramics International, 38(1): 277-282.

[6] H. Kungl, T. Fett, S.Wagner, M.J.Hoffmann. (2007) Nonlinearity of Strain and Strain Hysteresis in Morphotropic LaSr-Doped Lead Zirconate Titanate Under Unipolar Cycling With High Electric Fields[J]. J. Appl. Phys, 101 (4): 044101-1-044101-9.

[7] H. Kungl, R. Theissmann, C. Baecht, M. Knapp, H. Fuess, S. Wagner, T. Fett, and M. J. Hoffmann, (2007) “Estimation of Strain From Piezoelectric Effect and Domain Switching in Morphotropic PZT by Combined Analysis of Macroscopic Strain Measurements and Synchrotron X-ray Data,” Acta Mater., 55, 1849–61.