TRANSPARENT PLZT CERAMICS AND THEIR PRACTICAL USE

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Piezoelectric ceramics lead zirconate titanate (PZT) is a material of high technological importance due to its applications in solid-state actuators, transducers and sensors. La^{+3} ion can be substituted for Pb^{+2} ion in PZT system (as called PLZT) because of its similar ionic sizes. This paper summarizes properties of transparent PLZT ceramics and their practical use.

INTRODUCTION

Lead zirconate titanate (PZT) ceramics with variable Zr/Ti ratios have been shown to exhibit a variety of ferroic phases such as ferroelectric (FE), antiferroelectric (AFE) and paraelectric (PE) phases. Ferroic materials have active domain walls, that is, crystallographic boundaries that can be moved by applying an external force or field. Due to this advantages, PZT ceramics have received much attention of researches of all over the world [1-5]. It is well established that substitution of La³⁺ at the Pb-site of PZT (abbreviated as PLZT) gives improved piezoelectric and opto-electronic properties of the materials due to the high solubility of La in PZT, reduction of distortion in perovskite structure in PLZT and formation of high density samples. It is most interesting to observe diffuse phase transition (DPT) in complex PLZT [6-7].

1. PLZT CERAMIC MATERIALS

PLZT ceramics is a family of transparent oxide electro optic ceramic materials. Their crystallography structure is perovskite type with the formulation of ABO₃. The PLZT formula $(Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3)$ assumes that La substitutes for Pb²⁺ in the A-site and the B-site vacancies are created for electrical balance. The PLZT composition is conventionally abbreviatedas x/y/1-y, by which a PLZT 20/50/50 composition means a La concentration of 20 at. % with a Zr/Ti ratio of 50 to 50.



Fig.1 Perovskite cell of PLZT

The figure 2 shows samples of the transparent PLZT type ceramics which were obtained by the hot pressing method. The thickness of these samples is about 1 mm.



Fig.2 Transparent PLZT ceramics

On the figure 3 shown the phase diagram of PLZT ceramics [8]. Electro-optic compositions in the PLZT phase diagram are generally divided into three application areas: quadratic, memory and linear.



Fig.3 Phase diagram of PLZT at room temperature [8]

The quadratic materials are compositionally located along the phase boundary separating the ferroelectric and paraelectric phases, principally in the crosshatched area. Memory compositions having stable, electrically switchable optical states are largely located in the ferroelectric (FE) rhomboedral phase region, and the linear materials possess non switching, linear electrooptic effects are confined to the area encompassing the tetragonal phase. A less studied composition region is the antiferroelectric (AFE) phase near the PbZrO₃ side of the phase diagram.

Ferroelectric ceramics are traditionally made from powders formulated from individual oxides; however, for PLZT materials powders made from a chemical coprecipitation technique is more appropriate. Understandably, the PLZT ceramics require a higher purity, more homogenous, and high-reactivity powder than other non-optic materials because inhomogeneities is much more sensitive optically than electrically.

The microstructure of the sintered samples is shown in figure 4. The nature of microctructure suggests the formation of the single-phase compounds. Also from the micrographs it is clear that the grains are uniformly distributed over the entire sample surface and densely packed. The grains are almost of same shape except a few in the columnar shape, which may be due to the presence of some liquid phase during the high temperature sintering process. The average grain size of the samples is found to be $3.0 - 4.0 \mu m$. The SEM images from the crack of the samples have been made in Laboratory of Field Emission Scanning Electron Microscopy and Microanalysis at the Institute of Geological Science of the Jagiellonian University.



Fig.4 SEM images of 20/50/50 PLZT ceramics

2. DEVICES MADE FROM PLZT CERAMIC MATERIALS

There is many possibilities of uses of the PZLT ceramics, range of uses depends on way of obtaining method (for example: solid state solution from oxides or sol-gel method) and shape of final material (thin film or 'normal' samples).

Through many years since PLZT ceramics were obtained, most of the attentions have been paid to the potential application of the ferroelectric thin films with integrated semiconductor devices. This includes high permittivity films for capacitors in ultra-high density dynamic random access memories (DRAMs) [9]. For the next-generation DRAMs, a very high density memory cell is required, in order to maintain acceptable die size. Consequently, the planar storage capacitor area will be reduced. It is, therefore, essential to increase the charge storage density of capacitors, to maintain adequate signal margins. In general, a high permittivity allows for a high charge storage density. Materials for DRAM capacitors must also possess a high dielectric strength and a low leakage current [10].

Tetragonal PLZT films with large tetragonality exhibit polarization fatigue behavior even at 10^5 cycles [11]. This fatigue behavior results in degradation of electrical properties such as a decrease in the dielectric constant and polarization. Pseudocubic PLZT films exhibiting minimized hysteresis and relaxor behavior [12] are, however, more useful for thin

film capacitors because their structural and electrical properties are quite different from those of normal ferroelectrics.



Fig.5 The prototype of the PLZT memory

From the point of view of the DRAMs capacitor application the PLZT with ratio Zr/Ti 50/50 with 14% at. of lanthanum is the best. The thin film which contains 14 % at. La exhibited higher permittivity at room temperature, allowing a high charge storage density; 18 μ C/cm² [13].

Possibility of uses of the PLZT ceramics as a result of the photostriction phenomena. First of all what is few word about this phenomena. Photostriction is the light induced strain in a material, which can also be regarded as the superposition of photovoltaic and converse-piezoelectric effects [14]. Materials exhibiting photostrictive effect are of interest for their potential usage in new types of actuators such as wireless remote control photo-actuators.



Fig.6 Photostrictive actuator element PLZT

The possibility of directly producing strain by light illumination without any electrical lead wire connection makes them very attractive for micro-actuator and micro-sensor applications. Flexible microactuators based on tailored films of photostrictive PLZT with respect to the sample thickness and surface characteristics on flexible substrate have high potential for a substantial enhancement in the photoactuation efficiency. This flexible

actuators can be used in bio-morphic explorers for future spacemissions as proposed by Thakoor et al. [15].



Fig.7 The wavelength dispersion of the absorption of PLZT

Adaptive space structures which can be controlled by the illumination are some of the possible and intriguing applications. These materials are also promising for the photo-acoustic device of the optical communication system, such as photophone [16].



Fig.8 PLZT high speed optical shutter

Figure 8 shown high speed shutter time of response is $5\mu s$ (about 200 kHz), electrostatic capacity $0.1\mu F$ and area of shutter $10x10 \text{ mm}^2$.

Simple PLZT ceramics electrooptic (EO) modulators seem to be the best alternative to replace the dangerous nitrobenzene Kerr cells used before in schools and universities for demonstration of the EO effect and data transmitting via the low intensity He-Ne laser beam.



Fig.9 Schematic diagram of PLZT modulator [17]

Modulators with the aperture 8x1.5 mm and the optical path only 1.5 mm taking into account the simplicity of their adjusting are attractive also for use with other lasers such as the more powerful Ar+ ion laser. Ar+ laser causes, at first, some heating of the modulator due absorption losses, and secondly, so called "optical damage" effect (photorefraction). The high enough intensity of the beam releases in PLZT charge carriers which migrate within the illuminated region. That creates the space electric field (the screening field), which can freeze after interrupting of illumination or switching off the electric field. The screening electric field can cause the change of the birefringence induced by the applied electric field, and create the remanent birefringence [17].

3. CONCLUSIONS

Modification of the PZT system by the addition of lanthanum sesquioxide has a marked beneficial effect on several of the basic properties of the material, such as increased squareness of the hysteresis loop, decreased coercive field, increased dielectric constant, maximum coupling coefficients, increased mechanical compliance, and enhanced optical transparency. Many possibilities of uses of the PLZT system have been shown, such as thin films for capacitors in ultra-high density dynamic random access memories (DRAMs), new types of actuators as wireless remote control photo-actuators, high speed optical shutter, modulators, the photo-acoustic device of the optical communication system. These possibilities makes these materials very attractive both present and future uses. The PLZT ceramic materials are presently uses in such different branches of our daily life as electronic, optic, medicine, communication and new possibility still waiting for discovery.

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