

RECENT ADVANCES IN LEAD-FREE PIEZOELECTRIC MATERIALS

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ABSTRACT

This brief review article plans to summarize the current advances in lead-free piezoelectric materials. The search for lead-free substitutions to $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ piezoelectric ceramics (PZT) has turned out to be a main topic in functional materials research due to legislation in many countries that confines the use of lead alloys and compounds in commercial products. The present paper scrutinizes both the requirements for guidelines and the implications those regulations have created in the context of piezoelectric materials. This article also discusses the toxicity of lead, defines the existing regulation to restrict the spread of lead in the environment. Also, some potential materials which are alternatives to PZT are discussed.

Keywords: Lead-free; Piezoelectric; Titania-Based Piezo-electricity

I. INTRODUCTION

The previous decade has perceived much curiosity in the potential development of a non-lead substitute to the lead-based electro-ceramics, which presently lead the market for piezoelectric devices. The ecological and health threats of lead are well studied and documented. In other sectors, lead use diminishes but currently a practical lead-free piezoelectric material has until now not been found, and the snowballing demand for high-performance piezoelectric materials means that lead use is a mounting concern.

Even though the barium titanate (BTO) was the foremost ferroelectric ceramic to be used for its piezoelectric characteristics, it was not largely used in any applications and it is surpassed by the perovskite lead zirconate titanate $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) a material with incomparable piezoelectric properties and a high-dielectric constant that enables the PZT use for piezoelectric applications presently. $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ is characteristically prepared by the mixed-oxide way from starting powders, and compositionally, most $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics lie near a morphotropic phase boundary separating tetragonal and rhombohedral stages [1].

In this regard, the crucial and functional characteristics of the piezoelectric materials is electromechanical coupling coefficients and permittivity peak. Additionally, PZT used in range of potential applications due to its band gap engineering by doping with certain donor and acceptor dopants, which allow the manufacture to fabricate the soft and hard PZTs materials separately.

This aspect significantly surges the usefulness of PZT, with soft ceramic displaying enhanced piezoelectric constants and coupling factors. But actually easy to depolarize, whilst hard ceramics have moderately poor piezoelectric characteristics. The large value of coercive field is more problematic to depolarize and have very low dielectric losses, enabling these materials for more real-world and certain applications [2].

The yearly global manufacturing of lead is roughly 4.7 million tons and is beat by recycled lead production at 6 million tons. Out of this quantity, close to 0.015% of the lead used in the manufacturing of PZT devices. The mining of lead results into the generation of large amounts of waste. A significant portion of lead mining takes place in developing countries, which already affected by the low environmental awareness and health standards. The manufacture of lead reasons for noteworthy degradation of the environment. It is observed that the lead smelters during their process release significant amount of Cd and Pb into the atmosphere and yield into the gas pollution. In these circumstances, families breathing and residing close to mining and procedure operations are at certain risk.

In grown person, the key cause of lead poisoning is work-related exposure. Therefore, government imposes restriction on the most industrial jurisdiction and workplace where lead related work is happened. In USA, Occupational Safety and Health Administration permitted exposure limit for lead is $<50 \mu\text{g m}^{-3}$ in air over 8 h and actual action limit is $30 \mu\text{g m}^{-3}$. Exceeding this value, the plant manager obligation act to decrease the exposure.

In developed nations and lead exporter nations, the health and safety related departments in the workplace and environmental protection from industrial procedures are well structured and supervised by national agencies. Best practices in risk assessment and moderation are extensively surveyed, and consistent monitoring of workforce blood lead levels confirms that these actions have been operative.

The jeopardy of work-related lead poisoning due to the production of PZT in developed nations and lead exporter nations is extremely low. On other hand, the success of parallel procedures in developing nations is noticeably inferior [3].

II. ENVIRONMENTAL IMPACT OF PZT MATERIALS

Piezoelectric materials based on PZT are used in range of application including actuators, sensors and transducers. Presently, the cognizance to the environmental and health hazards effects of lead are growing. Main shortcoming associated with PZT based piezoelectric materials is that it comprises more than 60 wt% lead as a toxic heavy material. During the PZT materials' life-cycle, more amount of lead oxide and lead zirconate titanate is released into the atmosphere. The considerable amount of lead oxide released during the heating process. Unused material is also generated during the various process, which creates the issue of recycling and waste disposal. The devices-based lead-based piezoelectric materials facing the issues of recycling and disposing, which are used in large quantity by cars, sound equipment and medical devices. The legislation of European Union in 2003 recommended that the PZT based piezoelectric materials should replace by lead-free materials. As an outcome of this resolution, Restriction of Hazardous Substances Directive implemented in European Union from 2006. This limits the usage of lead in the production of many kinds of electrical devices. The raising interest of sensors and actuators in various medical related application, lead free piezoelectric are very much useful. Presently, scientific community facing the issues in development of lead-free piezoelectric materials in attaining equivalent piezoelectric characteristics displayed by PZT. But in practical, the available lead-free piezoelectric materials show the weak piezoelectric performance in various applications. The potential substitute to the PZT and an example of lead-free piezoelectric material is LiNbO_3 , which was first discovered in 1949 as ferroelectric material as useful for piezoelectric and electro-optic properties [4].

III. POTENTIAL LEAD-FREE PIEZOELECTRIC MATERIALS

3.1 Bismuth Layer Structured Ferroelectrics (BLSF)

Polycrystalline ferroelectric piezoelectric materials are extensively used in numerous practically useful electronic devices. The recent reports available in literature related to piezoelectric properties of bismuth layer-structured ferroelectrics polycrystals are indicate that bismuth layer-structured ferroelectrics are the potential candidate as lead-free piezoelectric material for the piezoelectric application. During literature survey it is observed that the longitudinal polarization stretching and in-plane polarization rotation play vital role in the many piezo-electricity for poled polycrystalline materials. Also, it is reported that the polarization widening of Bi_2O_2 layer and sliding between Bi_2O_2 layer and perovskite block are exposed. These effects show an imperative role for the piezo-electricity of bismuth layer-structured ferroelectrics.

Piezoelectric characteristics of conventional bismuth layer-structured ferroelectrics ceramics are not considerable compared to the single crystals. The key reason for low piezo-electric action in these ceramics are attributed to the two-dimensional constraint on the allowable rotations of the natural polarization by electric poling. The ferroelectric ceramics that have grain crystallites exhibits the lower crystal symmetry as bismuth layer-type compounds. Figure 1 shows the crystal structure of bismuth layered structure ferroelectric [5].

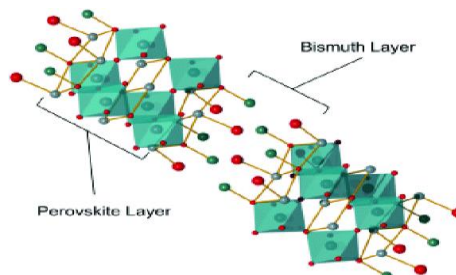


Figure 1. Crystal structure of bismuth layered structure ferroelectric.

3.2 Barium Titanate (BaTiO₃-BT)

The barium titanate crystal was first oxide with perovskite-type structure developed between 1940s to 1950s, which possess the ferroelectric characteristics. The barium titanate possesses the moderately high electromechanical coupling factor and has been moderately used for piezoelectric applications such as sonar. It is mainly used for the capacitor applications due to its very high permittivity of pure barium titanate prepared by solid-state method. Still, barium titanate shows a comparatively low Curie temperature, restricting the working temperature range and restrictive their use in piezoelectric applications. The entire scientific community putting lot of efforts to improve the piezoelectric characteristics and to rise the transition point T_c, there has not been much of an accomplishment. The barium titanate is frequently used in solid solution with other lead-free compounds to form an morphotropic phase boundary that improves the piezoelectric and dielectric properties. Figure 2 depicts the barium titanate crystal [6].

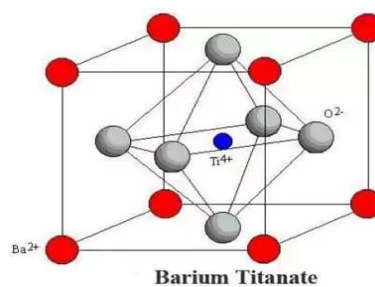


Figure 2. Barium Titanate Crystal.

3.3 Sodium Bismuth Titanate - (Bi_{1/2}Na_{1/2})TiO₃ - (BNT)

Sodium bismuth titanate was first reported around the 1960s by Smolenskii research group. Sodium bismuth titanate achieved large interest due to the topical rush in lead-free material advances in the past two decades. Sodium bismuth titanate is a perovskite-type ferroelectric material at room conditions and displays relaxor ferroelectric behavior. In Sodium bismuth titanate, diffused phase transformation phenomenon is observed in the temperature range 200-300 °C due to a transition from the rhombohedral to tetragonal symmetry. Sodium bismuth titanate is good ferroelectric material with a moderately huge remnant polarization at room conditions. Due to large remnant polarization at room conditions and a moderately high Curie temperature enable sodium bismuth titanate as possible candidate to replace PZT based piezo-electric materials. Figure 3 shows the crystal structure of sodium bismuth titanate [7].

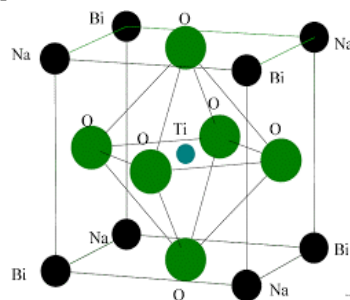


Figure 3. Crystal structure of sodium bismuth titanate.

IV. CONCLUSIONS

Environmental regulations flourished in substituting lead and lead based materials in a numerous applications like paints, solder and a diversity of electronic components. Excused from this prohibition of lead are applications and technologies where no appropriate substitution is still existing, such as piezo-electric materials for various applications including the sensors and transducers. The characteristics of various lead-free piezo-electric materials have its place to the bismuth layer-structured and perovskite ferro-electric materials are discussed in this brief review. Whereas not a single material of the currently existing non-lead piezoceramics can contest with PZT, which can be considered as substitutes to PZT for superior applications.

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