Emergence of environmentally friendly piezoelectric material

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The article mainly focuses on the application of the most popular piezoelectric material PZT and its detrimental effects on the environment, the rise of environment friendly piezoelectric materials and recent research and development works on them.

Piezoelectricity is a reversible property possessed by a selected group of materials that does not have a center of symmetry. When a dimensional change is imposed on the dielectric, polarization occurs and a voltage or field is created which is known as direct effect. On the other hand, the application of an electric field to a dielectric may also result in dimensional change which is known as inverse effect. Dielectric materials that display this reversible behavior are piezoelectric.

The phenomenon was first discovered in 1880 when Pierre and Jacques Curie demonstrated that when specially prepared crystals (such as quartz, topaz, and Rochelle salt) were subjected to a mechanical stress they could measure a surface charge [1]. A year later, Gabriel Lippmann deduced from thermodynamics that they would also exhibit a strain in an applied electric field. The Curies later experimentally confirmed this effect and proved the linear and reversible nature of piezoelectricity.

One of the initial applications of the piezoelectric effect was an ultrasonic submarine detector developed during the First World War. The continued development of piezoelectric materials has led to a huge market of products ranging from those for everyday use to more specialized devices. Some typical applications are:

Industry	Application
Automotive	Air bag sensor, air flow sensor, audible alarms, fuel atomizer, keyless door entry, seat belt buzzers, knock sensors.
Computer	Disc drives, inkjet printers.
Consumer	Cigarette lighters, depth finders, fish finders, humidifiers, jewellery cleaners, musical instruments, speakers, telephones.
Medical	Disposable patient monitors, foetal heart monitors, ultrasonic imaging.
Military	Depth sounders, guidance systems, hydrophones, sonar.

Figure 1. Piezoelectric air transducer used as automobile sensor

Figure 2. Piezoelectric actuators used as accelerometer

The most widely used of all piezoelectric ceramics, known by the acronym PZT is actually solid solutions between lead zirconate (PbZrO3) known as PZ and lead titanate (PbTiO3) known as PT. It is used on a wide scale mainly due to its unique properties at the morphotropic phase boundary (MPB), at a composition where the PZ : PT ratio is almost 1 : 1, as shown in figure-5. PZT compositions near the MPB have both high Σ_r and high K_p as shown in Figure-6.This is mainly due to the fact that polarization of the PZT solid solution at the MPB composition may easily switch between ferroelectric tetragonal and ferroelectric rhombohedral phase, effectively resulting in 14 available equivalent polar directions.

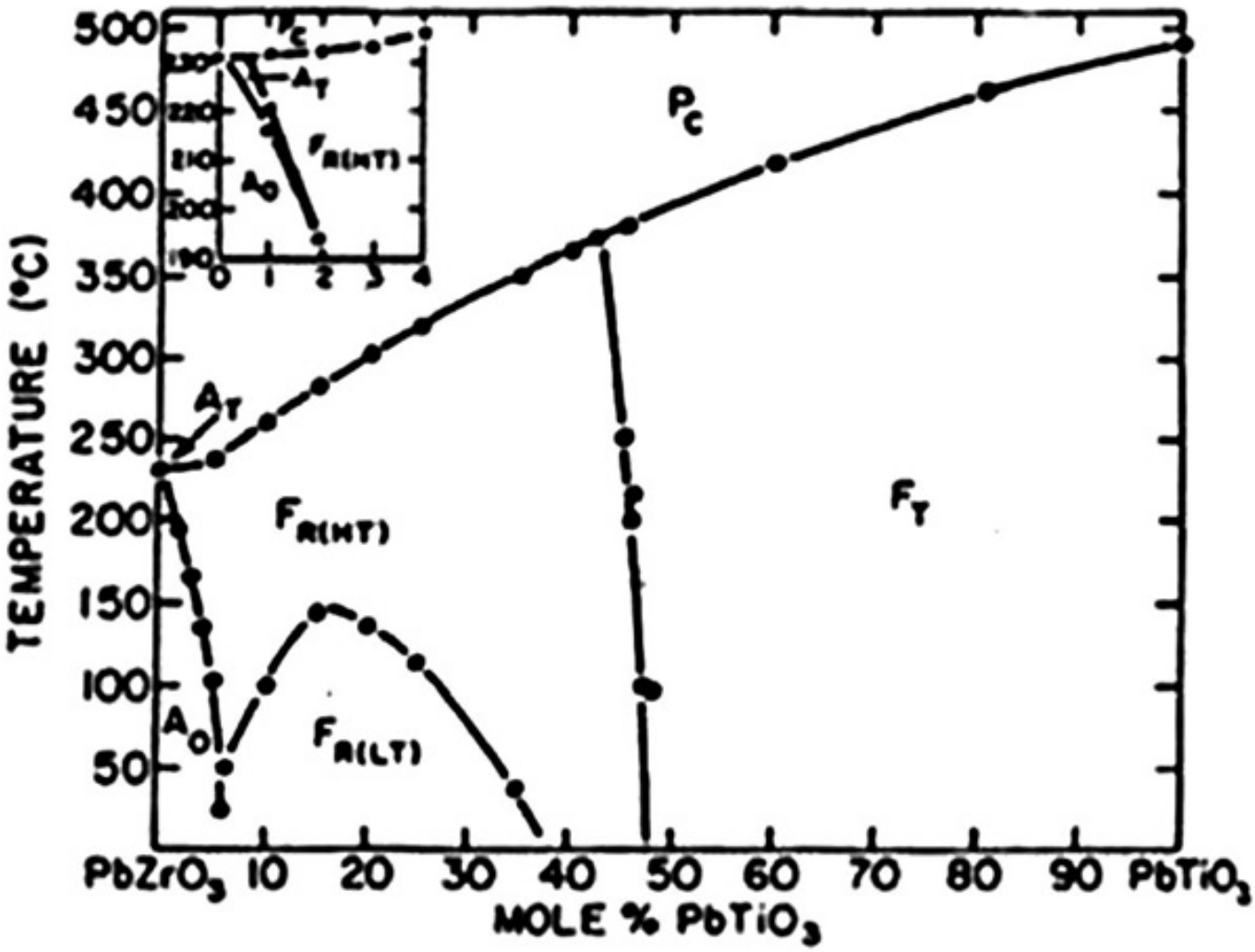

Figure 5. The PZT phase diagram [2]

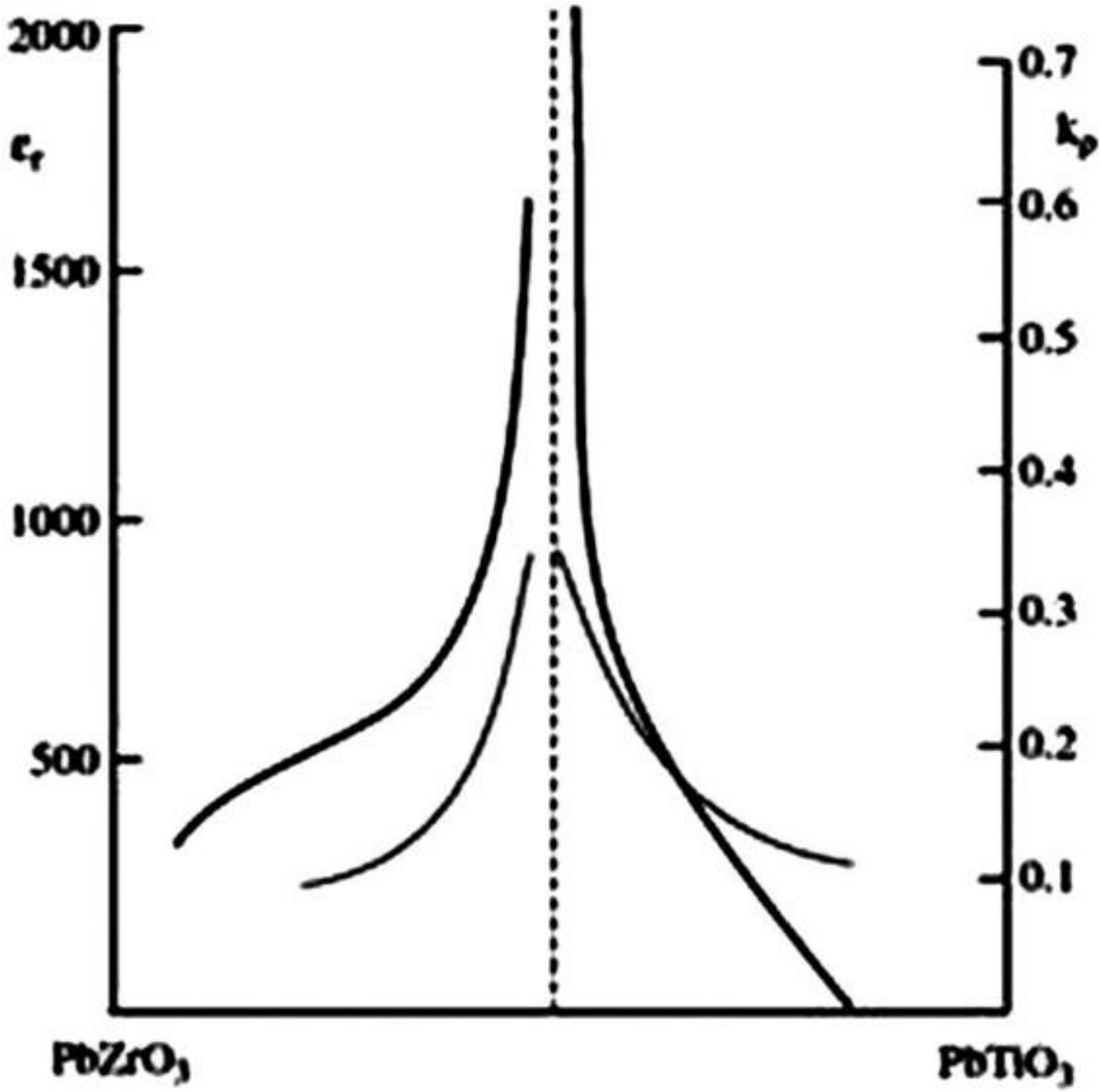

Figure 6. Dielectric constants and coupling coefficients for PZT composition near the MPB [2]

However, lead and its compounds are generally toxic. Lead poisoning has long been considered as an environmental health hazard, for its adverse effects on intellectual and neurological development. The important symptoms of lead poisoning on humans include fatigue, aches in muscles and joints, abdominal discomfort etc. Lead can also affect the genetic transcription of DNA by interaction with nucleic acid binding proteins [3]. As a result, several classes of materials are now being considered as potentially attractive alternatives to PZT for applications like sensors, actuators etc.

There are several candidates of lead-free piezoelectric ceramics: Bi-based piezoelectric ceramics such as perovskite-type $(Bi_{0.5}A_{0.5})TiO_3$ (A = Na, K) ceramics, $M_2NaNb_5O_{15}$ (M = Sr, Ca, Ba) ceramics, BaTiO3 ceramics, Alkaline niobate-based

perovskite-type ceramics [4]. Among those several candidates of lead-free piezoelectrics, alkaline niobate-based perovskite type ceramics are promising candidates for lead-free piezoelectric materials and most recent studies have concentrated on the development of KNN-based lead-free ceramics [5-7].

KNN has a lot of potential as a lead free piezoelectric material because similar to PZT it also exhibits MPB. KNN exhibits three morphotropic phase boundaries (MPB) as shown in figure-7, located at around 52.5 mol%, 67.5 mol% and 82.5 mol% $NaNbO_3$ (marked by the dash lines), separating two different orthorhombic phases, respectively.

However, it has been reported by Egerton and his coworkers that piezoelectric properties of KNN are relatively poor [3]. Whereas the piezoelectric properties of PZT are (d_{33}=374 pC/N, k_p=0.67), the maximum piezoelectric performance of KNN exhibited at MPB near 50 mol% $NaNbO_3$, are (d_{33}=80 pC/N, k_p=0.36); because the room temperature phase of KNN is ferroelectric orthorhombic, which has only 12 polar axes. Moreover, there are some processing difficulties that prevent achievement of high piezoelectric properties. For example: Due to volatility of the potassium element and instability of the crystal phase, it is difficult to obtain a sintered body with a high density by conventional ceramic process and pressure-less sintering [4]. Therefore, additional quantity of potassium needs to be added during preparation using solid solution method.

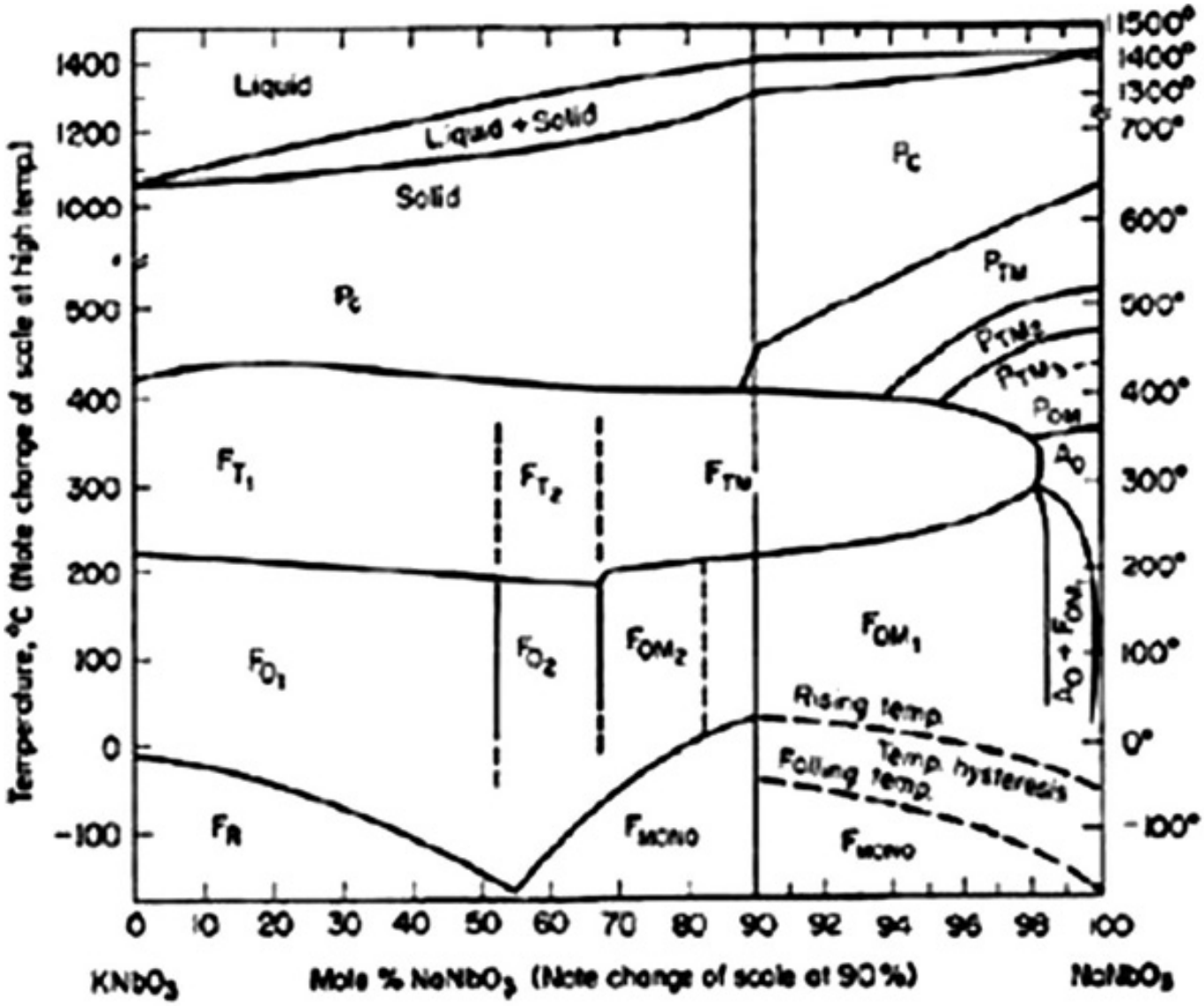

Figure 7: The KNN phase diagram [3]

As a result, recent research and development work focuses on developing numerous alternative strategies to solve this problem and these strategies can be summarized into three categories [4]. Firstly, sintering of dense KNN ceramics by special sintering methods, such as hot pressing and spark plasma sintering [8-9]. Secondly, the formation of a new solid solution by adding other perovskite compounds, such as $BaTiO_3$, $SrTiO_3$, $LiNbO_3$, $LiSbO_3$, and $LiTaO_3$ which transforms the phase diagram of $KNbO_3$-$NaNbO_3$ and enhances the phase stability of KNN ceramics. Finally, addition of novel sintering aids such as $K_4CuNb_8O_{23}$, $K_{5.4}CuTa_{10}O_{29}$, ZnO, and CuO to KNN ceramics, which lowers sintering temperature of KNN due to the formation of liquid phase during the sintering.

In one study, a small amount of $K_{1.94}Zn_{1.06}Ta_{5.19}O_{15}$ (KZT) compound was added to KNN ceramics with the expectation of improving KNN sinterability due to the ability of the potassium element in KZT to compensate for K2O evaporation of KNN during the sintering process and the recognized function of zinc as a good sintering aid capable of improving piezoelectric properties. In case of pressure-less sintering, KZT lowered the sintering temperature from 1115°C to 1070°C. Moreover, at around

2mol% KZT, % theoretical density reached as high as 98%. All these had a positive impact on the piezoelectric properties (d_{33}=120 pC/N, k_p=0.45). So, the small amount of addition of KZT was effective in improving the sinterability, dielectric, and piezoelectric properties of KNN ceramics [10].

In another study, polycrystalline samples of Lead free $(K_{0.5}Na_{0.5})_{1-x}(Li)_x(Sb)_x(Nb)_{1-x}O_3$ ceramics with nominal compositions (x = 0.040 to 0.060) were prepared by high temperature solid state reaction technique. In this case, normal sintering process yielded compounds with density around 98.2% of the theoretical value where the samples were sintered between 1060°C - 1120°C [11].

Recent research and development works focus on developing lead free piezoelectric materials specially KNN to be used for actuator and transducer technologies. There is a huge scope for research in this field. This review will provide a guideline for further development.

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