Silver Niobate Based Antiferroelectric Ceramics for High Energy Storage Density Applications: Review

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Abstract **-Dielectric materials show fast charging and discharging capability and have high power density. Among dielectrics, antiferroelectric (AFE) materials provide a very good option due to their enhanced energy density. Primarily, Pb based ceramics were used as AFE materials for energy storage applications. But due to toxic nature of Pb, it is hazardous for our environment. So, it was required to develop a lead free AFE material which will serve as a promising solution for High energy storage applications. This requirement led to development of Silver Niobate $AgNbO_3$ based AFE Ceramics. This review paper presents summary of use of Silver Niobate based AFE materials for High energy storage applications.**

INTRODUCTION

Due to the ability of fast charging and discharging, in addition to high power density, dielectric materials are in great demand [6,7,8] for high energy storage applications. To meet the requirements of miniaturization and integration of modern electronic industry, energy storage density of dielectrics needs to be increased. Among dielectrics, we have a variety of materials which can be used to fabricate electrical capacitors. These include linear dielectrics [10], ferroelectrics [11,12], relaxor ferroelectrics [9,13] and anti-ferroelectrics. Polarisation versus electric field (P-E) Hysteresis loop [5] of each of these classes of material is shown in fig.1. [5]

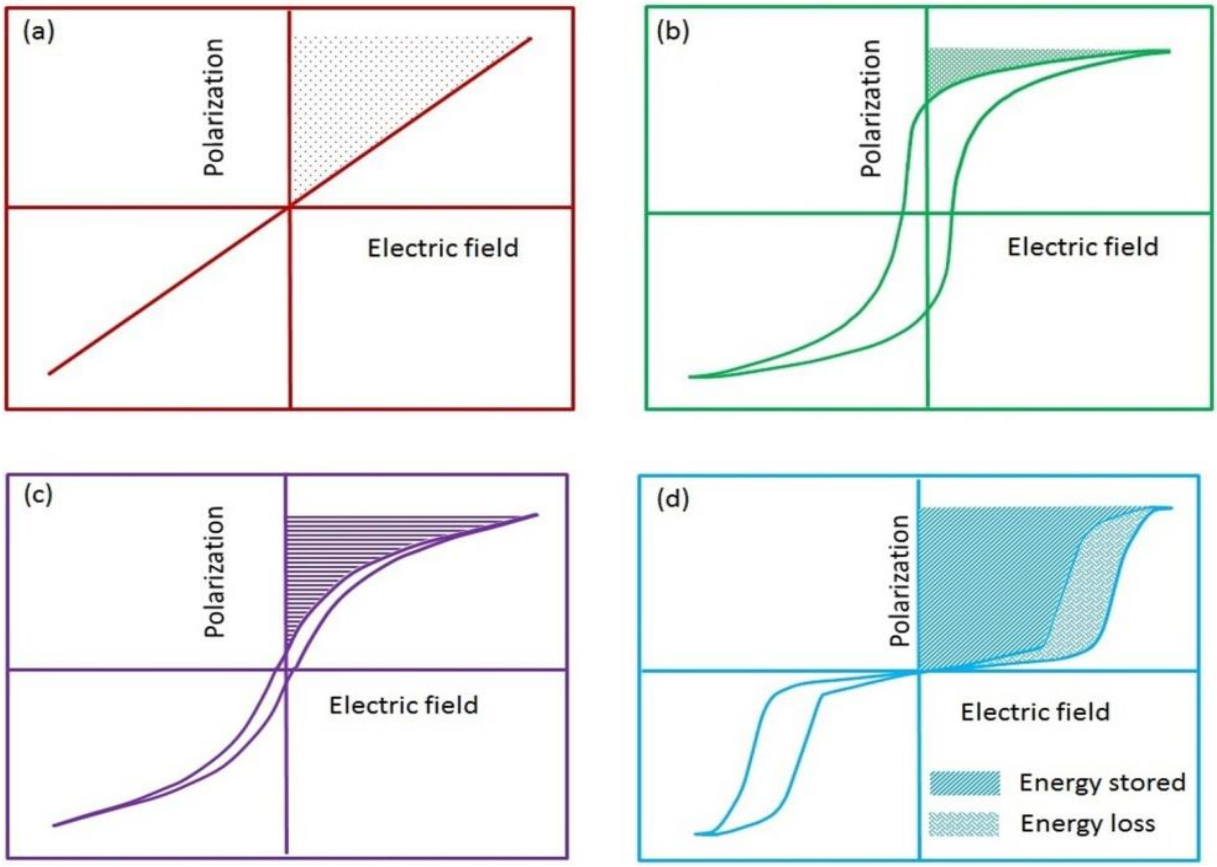

Figure 1. Figure represents the typical polarization versus electric field (P-E) hysteresis loops and energy storage characteristics of the four classes of solid dielectric materials namely (a) linear; (b) ferroelectric; (c) relaxor ferroelectric; (d) anti-ferroelectric (demonstration only; not to scale).[5]

This P-E loop can be used to determine the energy storage efficiency of material. In P-E loop, the dischargeable energy is represented by hatched area and dielectric loss is represented by the area within Hysteresis loop. The energy storage efficiency of corresponding material then can be calculated by taking the ratio of these two types of energies. Fig. 1(a) [5] represents hysteresis loop of linear dielectrics. They have low dielectric constant and their electric breakdown strength is high. Fig. 1(b) [5] corresponds to ferroelectrics characterized by large dielectric constant. But they have drawbacks of small dielectric breakdown strength and large dielectric losses. Relaxor dielectrics have negligible remanant polarization, coercivity and show absence of conceivable ferroelectric hysteresis as shown in fig. 1(c) [5]. So, they can serve well for energy storage capacitor applications [17,18]. But most of relaxor dielectrics are lead based. So, they are not a good option owing to the toxic nature of Pb, which harms the environment. We require a better lead-free solution for this application. Fig. 1(d) [5] shows P-E loop for Antiferroelectric materials which are a promising candidate for high energy density storage applications and are environment friendly too. They have low value of remanant polarization, low coercive electric field, high energy storage density and fast discharging rate due to FE to AFE phase transition [19,20]. Adjacent dipoles are aligned in anti-parallel directions in the innate state of Antiferroelectric materials [14,21,22]. This results in lack of any observable pyroelectric, ferroelectric or piezoelectric properties. At very low values of applied electric field, AFE materials do not show any considerable hysteresis because of absence of ferroelectric domains. They possess low coercive field, low remanant polarization and low dielectric loss. When electric field is increased beyond a certain value, dipoles rotate and align themselves in the direction of applied electric field [15,16] and now AFE material starts behaving as a ferroelectric material. But this change is reversible because when the applied electric field is reduced below the critical value, ferroelectric phase is again transformed into Antiferroelectric phase [20,23]. This loss of ferroelectric property at low value of electric field is responsible for fast discharging ability in AFE ceramics. Moreover, low value of hysteresis losses along with reversible AFE to FE phase transformation provides great opportunities for realization of high power and energy density in AFE ceramics. [14,24,25]

Basic information about structure and phase transitions in Silver Niobate ($AgNbO_3$)

In $AgNbO_3$ has perovskite structure as shown by studies. In $AgNbO_3$ ceramics, a number of phase transitions take place with increase in temperature.

$$M_1 \xrightarrow{67^0C} M_2 \xrightarrow{267^0C} M_3 \xrightarrow{353^0C} O_1 \xrightarrow{361^0C} O_2 \xrightarrow{387^0C} T \xrightarrow{579^0C} C$$

Here, M_1, M_2, M_3 represents orthorhombic phases in rhombic orientation. O_1, O_2 denote orthorhombic phases in parallel orientation. T represent tetragonal phase and C indicates cubic phase [29,30]. The transitions M_3- O_1, O_2- T and T-C which are governed by high temperature are related to the tilting of oxygen octahedron [31-33]. While the transitions among orthorhombic phases M_1, M_2 and M_3 are associated with the displacement of cation (Ag and Nb) [31,32]. Here, M_1 is ferrielectric (FIE) phase while both M_2 and M_3 are disordered AFE phase [28,34]. Due to ferrielectric structure at room temperature, Silver Niobate ceramics possess non-zero remnant polarization P_r . This P_r increases on application of high electric field thus affecting the energy storage density in a negative manner [35]. Change in composition affects behaviour of phase transitions and associated properties and plays an important role in energy storage density of Silver Niobate based ceramics [3].

FACTORS AFFECTING ENERGY STORAGE DENSITY IN ANTIFERROELECTRIC MATERIALS

AFE materials that exhibit double hysteresis loops proved to be a potential candidate for high energy storage density as compared to ferro electrics and linear dielectrics. The equation $W_{rec}=\int_{Pr}^{Pmax} Edp$ can be used to calculate the recoverable energy density (W_{rec}) for AFE materials. In this equation, E represents applied electric field and P_r and P_{max} are the remanant and maximum polarization respectively. Here, dielectric breakdown strength E_b of material puts a limit on value of applied electric field E. Thus, W_{rec} depends on E, P_r and P_{max}. There are certain other parameters also which are related to energy storage properties. These are forward switching (AFE-FE) field E_F, backward switching (FE-AFE) field E_A and switching hysteresis, $\Delta E=E_F$-

E_A. Thus, high P_{max}, E_F, E_A and low P_r in AFE material are required for ensuring large energy density. Also, there is a requirement of small ΔE to achieve high efficiency and high E_b is needed to apply high electric field to induce AFE-FE phase transition [3]. For perovskite structure (ABO_3), there is a tolerance factor (t) that can be used to determine their phase stability. $t=(R_A+R_O) / [\sqrt{2} (R_B + R_O)$, here Ro, R_A and R_B are respectively the ionic radii of oxygen anion, A-site cation and B-site cation. t>1 indicates stability of FE phase while t<1 supports stability of AFE phase [36].

This paper presents review of effect of different dopant on energy storage density W_{rec} in $AgNbO_3$ based ceramics depending on work carried out by Chenhong Xu et al [1], Lei Zhao et al [2] and Lei Zhao et al [3]

SPECIMEN FABRICATION AND CHARACTERIZATION TECHNIQUES –

Chenhong Xu et al prepared polycrystalline samples of AgNbO3, $Ag_{0.97}La_{0.01}NbO_3$, 0.3 wt %, Mn-doped $Ag_{0.97}La_{0.01}NbO_3$ by making use of conventional solid state reaction method[1].

Lei Zhao et al also used conventional solid state reaction process in order to prepare W - doped $AgNbO_3$ ceramics abbreviated as ANW_x, where x is 0, 0.1, 0.2, 0.3 wt % respectively [2].

Lei Zhao et al fabricated Ag $(Nb_{1-x}Ta_x)0_3$ abbreviated as ANT_x, where x is 0 ,5 ,10 ,15 and 20 mol % respectively by using conventional solid state reaction method [3].

In order to determine the crystal structure of specimen, X-Ray diffractometer was used. Grain size and microstructure were found using field emission scanning electron microscope (FE-SEM). Hysteresis loops were measured with the help of Ferroelectric measurement system at 1 Hz [1,2,3].

RESULT AND DISCUSSION

Chenhong Xu et al studied that under 1 KHz, the dielectric loss for $AgNbO_3$, $Ag_{0.97}La_{0.01}NbO_3$ and Mn doped $Ag_{0.97}La_{0.01}NbO_3$ was 1%,1.1% and 0.8% respectively. The dielectric loss is reduced effectively by Mn doping. P - E and I - E loops of pure AgNbO3 revealed that this structure has P_r = 3.9 μC/cm^2 after high electric field cycling. Also, the recoverable energy density W_{rec} was calculated to be 2.4 J/cm^3. Hysteresis loops of $Ag_{0.97}La_{0.01}NbO_3$ indicates increase in E_A from 52 kV/cm to 76 kV/cm thus indicating enhanced AFE stability. In hysteresis loops of Mn doped $Ag_{0.97}La_{0.01}NbO_3$, P_r was reduced to 1.8 μC/cm^2 and there was further increase in E_A to 86kV/cm, While P_{max} was reduced slightly to 39.6 μC/cm^2. This indicates the presence of complete antiferroelectric phase in structure. There are no local polar regions present now. Both the factors i.e. increasing E_A or decreasing P_r contribute positively towards enhancing energy storage properties of $AgNbO_3$ based ceramics. Chenhong Xu et al could achieve recoverable energy density W_{rec} as high as 3.2J/cm^3 in Mn doped $Ag_{0.97}La_{0.01}NbO_3$ due to codoping of La and Mn.[1]

Lei Zhao et al studied $AgNbO_3$ - x wt% WO_3 ceramics. Hysteresis loop of W - based ceramics shows an increase in integral area as compared to pure $AgNbO_3$. Higher P_{max} and lower value of P_r was seen in all W doped Silver Niobate ceramics in comparison to pure $AgNbO_3$. This resulted in an increase in P_{max} - P_r. Also, an increased E_F/E_A was also reported in W based $AgNbO_3$ ceramics. Both these factors played an important role in improving energy storage capability with W_{rec} > 3.0 J/cm^3 .The highest value of W_{rec} = 3.3 J/cm^3 was achieved in $AgNbO_3$ -0.1 wt % WO_3 ceramics. There was no further increase in energy storage density in samples with x= 0.2 – 0.3 wt % because of limited solubility of W^{6+} ions (less than 0.1 wt %). [2]

Lei Zhao et al reported that all Ag $(Nb_{1-x}Ta_x)$ O_3 ceramics possess a higher W_{rec} as compared to pure $AgNbO_3$. Hysteresis loops of Ag $(Nb_{1-x}Ta_x)$ O_3 solid solution indicate a larger integral area than that in pure $AgNbO_3$. It was found that P_{max} remained 35.5 – 37.2 μC/cm^2 for compositions of x = 0-15 mol % and at x = 20 mol %, it decreased slightly to 31.5 μC/cm^2. But important thing is that on addition of Ta, P_r was found to decrease while E_A and E_F show contrary trend making ΔE exhibiting the same values. Thus, substitution of Ta^{5+} for Nb^{5+} resulted in lower P_r and higher E_F/E_A thereby improving the energy storage density. W_{rec} 4.2J/cm^3 was achieved in Ag $(Nb_{0.85}Ta_{0.15})$ O_3 ceramics.[3]

CONCLUSION

Amongst AFE, Lead free Silver Niobate based antiferroelectric ceramics have proved to be an excellent alternative to lead containing AFE ceramics for large energy storage density applications. Addition of suitable dopant in the right composition can further enhance W_{rec} in $AgNbO_3$

based ceramics as compared to their pure counter parts. Present review indicates that a large energy storage density W_{rec} 3.2 J/cm^3 was achieved in Mn doped $Ag_{0.97}$ $La_{0.01}NbO_3$. Still higher value of Wrec = 3.3 J/cm^3 was achieved in AgNbO3 -0.1 wt % WO_3 ceramic. And highest value W_{rec} = 4.2 J/cm^3 was obtained in Ag ($Nb_{0.85}Ta_{0.15}$) O_3 ceramics.

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