

Physics of Functional Materials and Devices

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Lecture- 23, Week 6

Negative and Zero Expansion Ceramics

Welcome again in this second lecture of week 6. Let us continue our discussion on thermal properties of solids. You had a brief introduction in the previous lecture on the topic that is thermal expansion in solids and in today's lecture we will move towards thermal expansion in ceramics. What do we generally believe? We believe that whenever you heat a solid material it will have a positive thermal expansion that means its size will increase that is we a general believe we have, but today let us introduce to you a very interesting class of material that are negative or zero thermal expansion ceramics. After giving you examples of negative or zero thermal expansion ceramics, you will be introduced to a large number of applications where these ceramics are absolutely essential. These range from base applications to defense applications to even applications in electronics or microelectronics.

What is thermal expansion? What have we understood till now? We have seen that whenever a material is subjected to heat change or change in the temperature the dimension of the material changes that is you have a phenomenon where a material undergoes dimensional changes in response to the change in temperature. And why these changes take place because when you heat these materials the atoms or the constituents, they obtain higher vibrational energy and they vibrate more along their mean position. Now, if you have materials which are being heated and the atoms which constitute these materials then in these materials the vibrations would be higher. much higher, but in a given material you know that a lattice point is such that if you define a Wigner-Weitz seitz cell then what are you defining that there would be an area which belongs to a given atom and to it only.

So, the neighboring atom cannot influence this area of the atom, but if the vibrations increase then what is happening you start interfering in the Wigner Seitz cell or the first Brillouin zone of a given atom and that is not possible. So, what will happen again you will see that the atoms should move far away from each other so that they do not impinge or

they have interference zone associated to a given atom next to it. Now, the increased molecular motion leads to an average separation between the particles which is higher and that results in the expansion or increase in the volume. Now, expansion behavior of materials is governed by lattice constant that is what we meant. What is happening that if you consider the coefficient of thermal expansion that is how much the materials dimension will change per unit temperature change then you will find that this CTE can also be calculated by seeing the changes in lattice constants you can calculate the thermal expansions in solids.

So, mostly what are we doing? We are considering the bulk of the material. So, you see let us say a pen then you heat this pen you will see the expansion in the length and then you will calculate the thermal expansion in these solids. But there is another way of understanding the thermal expansion that is coefficient of thermal expansion which can be obtained by finding out the changes in the lattice constants itself. What are we considering till now? Let us say we consider ceramics, why ceramics? Mostly we are taking these materials which are insulators and they are inorganic and they have been prepared at high temperature. So, they are why high temperature consideration? So, that these solids have high density that is what we consider.

Consider in ceramics that you have densification taking place when you sinter the material that means you take the material to very high temperatures so that you can sinter the material and densify the whole structure. Now, when you change the temperature if you increase it. the vibrations in these atoms can increase or when you decrease the temperature the vibrations in these atoms can decrease and hence you can see positive thermal expansion in this case because even in the second case where you were decreasing the temperature you were seeing contraction. So, you had negatives on both sides. So, still the expansion coefficient was positive.

What is the next case that you increase the temperature, but you see contraction that is actually the negative thermal expansion. what have we seen expansion temperature increases you see expansion when temperature decreases you see contraction, but because both the signs are negative. So, you effectively still have the conventional expansion coefficient. Now, if you look into these materials, you will find that they are being used in industries ranging from electronics to high precision engineering. But why should we move to the new class of materials? that is negative or zero thermal expansion ceramics.

And can we correlate everything which we have studied till now that means, synthesis protocols, doping, changing of compositions, changing of composition leading to phase transformation investigation of lattice constants and determination of expansion coefficients in the level that is called as macroscopic or microscopic. That is you are talking as the material itself that is macroscopic or you are talking in terms of the atomic level that is microscopic. So, this is what we want to see today and let us start our discussion on these

materials which can actually combine with positive expansion coefficients and they can reduce the distortion or stresses which a system is going through if the temperature is varying. Let us take an example of a functional ceramic. We have been talking to you about perovskite type materials.

So, what is a perovskite type material? You have a site; you have an atom in the middle that is the B site and you have the oxygen at the phase centers. So, if you look into the cross-sectional view, this is what you actually see the arrangements of the atoms. structure. So, you have an ABO_3 structure. Let us take an example of a well-known negative thermal expansion ceramic and tell you how various things which have been taught to you till now is relevant.

So, what have we talked about? We have talked about synthesis and we have also talked about making modification in a parent by using a solvent or a solute that means you have a dopant going inside the parent matrix. So, we should also talk about doping and can this change the expansion coefficient properties of these materials. Let us take an example of lead titanate. which is a well-known negative expansion ceramic, but along with that we take an example of a system which is doped with calcium. So, we have lead calcium titanate the calcium concentration varies from that is x varies from 0 to 1.

So, you have the whole range which can be synthesized from lead titanate. If x is equal to 1 what will you get? If x is equal to 0 you get calcium titanate. So, the whole range is to be investigated. You can make this material using the protocol which is very simple and you can use a typical solid state synthesis route, very simple. And you will find that this is a protocol for which my team also holds a patent because People have been trying to make this material using solid state route, but they could not because they were getting a secondary phase getting stabilized.

The idea is that rather than calcining the material once we introduce the concept of second calcination under a lead atmosphere at 900° . So Why I mention this? You can play with the synthesis routes and you can get novel properties in materials. So, how do you make this material? You can take the starting raw materials at lead carbonate, calcium carbonate and titanium dioxide. So, one lead, one calcium, one titanium atom comes from here. Then you mix it in mortar pestle.

After that you take the powder and ball mill in a high energy ball mill for 6 hours using acetone as a mixing media. Because if you mix solids then what will happen when you are mixing it? you can get certain areas where one of the components may go and just get agglomerated, but when you have a wet sample then the mixing becomes much more uniform and homogeneous and therefore, acetone used as a mixing media and then you leave the whole slurry in air and acetone evaporates and you have the dried powder once again collect this powder in a petri dish you can heat it at 750° for 6 hours take it out again

ball mill so that you can break any preferred where one of the components have got agglomerated and then calcine it once again at 900° , but under lead oxide atmosphere. Why? Because beyond 700 lead becomes nascent that means lead may start leaving your material and that will lead to stoichiometric variation. So, you have to create a back pressure and that is what is done by putting lead oxide inside chamber where your powder is also going to be heated. So, because this is powder the lead will come out from this powder also and it will create a back pressure which will prevent the loss of lead from your sample.

After calcining the powder you can then break the agglomerated solid, pelletize it and then sinter it at 1200° for 6 hours to get a dense ceramic. There is a difference between calcination, sintering and annealing. Calcination is the temperature at which the reaction gets completed and the materials are formed. Sintering is the process which is densification of solids which were formed after calcination and annealing is a process where you ensure that you remove any preferred growth or any stresses in the sample when they are kept at certain pressure or they undergo certain physical measurements.

So, there are well defined definitions for these processes and you should understand the difference between the three. As you know as we talked about you have to then characterize these materials. You can clearly see this is an X-ray pattern of lead titanate which has a tetragonal cell with $P4mm$ unit cell. In comparison, you can see that calcium titanate has an orthorhombic $Pbmm$ cell and you can clearly see that the nature of the diffraction pattern in these two are quite different. So, if you have these two different materials combining together and their structures are quite different, you will expect that a new phase may get formed and you will have a new structure and if you have a new structure getting formed then the properties of that material would be different from that of lead titanate and calcium titanate.

So, you do that study once again. So, I have taken just a region which is a selected region of lead calcium titanate. So, you can go on changing the concentration 0.20 means what lead is 80 percent calcium is 20 percent.

0.50 means lead is 50 percent, calcium is 50 percent in this solid solution. You can clearly see that as you move from one composition to the other the nature of peaks are changing. If you just analyze this evolution of peak profiles, you do not have to do any complicated retwell refinement studies which some of you may have heard about. You do not have to go and do very complicated structural analysis. You can just plot them carefully and by analyzing the region which you are seeing.

Is the region where there are modulations in the peak intensity and profiles you can find out that there is a possibility or there is an occurrence of phase transition. In this you can clearly see that at a composition of around 40 . So, you can see this peak is nearly vanishing

when you go from 30 to 40. but there is some signature as a kink in the 200 peak of the unit cell, but this in high intensity peak vanishes. This indicates that there is a phase transformation taking place at this composition.

Similarly, if you go from 50 to 60 you can see that you have appearances of super lattice peaks again there is a phase transformation when you go from 50 to 60. So, there is a region where you have the tetragonal phase which is dominant then there is an intermediate region where there is a competing instability and this instability is coming in because the material can either go towards orthorhombic coming in from the calcium titanate end or it can go to tetragonal cell which is coming from the lead titanate end. Hence, there is a competing instabilities and you see a region where you have both O + T that is orthorhombic and tetragonal unit cells getting stabilized and beyond 0.60, you see materials which have predominant orthorhombic size. So, now you can clearly see that as a function of topping, you can get new phases stabilizing in a material, but all the peaks can be indexed with one or the other unit cell.

Hence, it is not an impure material, it is a solid solution. You do not see any impure purity peak. Now, let us see what happens. What is the origin of thermal expansion? If you consider let us, say a potential energy curve, let us say you have a potential energy curve $U(r)$ as a function of r . If you consider a symmetric potential energy curve, will you see thermal expansion in these materials? No, you will not see because let us say this is at T_0 .

Now, what is this point suggesting that you have a range where the material can vibrate when you go from T_0 to T_1 , but what do you mention what do you write as the lattice point you write as the mean position. So, if you have a symmetric curve. you go on increasing the temperature from one point to the other you will see that it the locus of these points would lead to a straight line and there is no variation, but when you have an asymmetric potential energy curve then only you see that the mean position changes So, you move away from a case where you would have expected if there would have been a symmetric curve to a point where you see that the final point and the initial points are very different and you have a slope associated with this curve. which gives you the expansion in solids. So, thermal expansion is a direct consequence of the deviation from symmetric curve to the asymmetric curve in $U(r)$ versus r that is the energy curve in solids.

So, you should understand the importance of the asymmetric potential energy curve very clearly because that is where the origin of expansion in solids lie. It is not that just when you heat a material that it starts to vibrate and therefore, you will get an expansion because if one material vibrates at a given temperature, then the phonons in the same material will have vibration at T_1 is equal to T_2 . Then also if you have a symmetric curve, you will only see the vibrations would increase, but the mean positions would not show any expansion. How do you measure the experimental value of the expansion in the materials that is the

macroscopic scale? you generally use dilatometry. So, what you have a typical dilatometry it is the LVDT based system.

So, what you have you have a furnace in which you will put your sample and, on the sample, you will put a push rod. So, you have a push rod which is enclosed inside a sample holder and when you increase the temperature of the surrounding in the sample, this push rod pushes the LVDT and the differential voltage change leads to the information about the change in length. So, you can then find out the change in length by the change in the voltage. So, this is a composition where you have, this is the composition. So, you can clearly see you go on increasing the materials temperature, then the material is contracting rather than expanding.

Why? We do not know still. Let us see why it will happen. But, after a given temperature it goes to the conventional positive thermal expansion type. You increase the temperature the material shows the normal positive thermal expansion. But then you go from 30 percent to 35 percent temperature. composition the magnitude change is much lower.

So, you see much lower change in the magnitude. So, you see very little expansion coefficient in the negative direction that is the negative thermal expansion. You go to 40 percent, you see nearly no negative expansion, but if you zoom the area, you will find that there is certain negative expansion, but the order is much lower you go to 45 percent there is no NTE. So, just by changing the concentration of calcium you have modulated the expansion coefficient not only that you have changed the nature of the expansion coefficient itself. And if you want to determine these values you can use the formulas which we mentioned in the previous class and you will find that you have different temperature regions and in different temperature regions you have various compositions which have varying thermal expansion coefficient.

So, obviously, it is clear. one material choose different compositions, you can get different expansion coefficients and if you have different expansion coefficients along with that you can change the sign of the expansion coefficient, you can use this material in different applications. that is the big advantage of lead calcium titanate. Along with that please remember it is already a material which is used as dielectric. So, you have a material which is used as dielectric, it is a typical ceramic. So, used as dielectric, it has expansion coefficients which can be tuned and it has different types of expansion coefficient and we had defined functional materials as the ones which can have at least two or more than two types of functionalities.

So, this material once again becomes an example of a functional materials. It is also important to understand why this crossover is taking place in the expansion behavior. This crossover is typically taking place because if you plot the variation in dielectric constant as a function of temperature, you will find that in this ferroelectric ceramic there is a phase

transformation taking place at the same temperature at which you see a crossover from NTE to PTE. So, if there is a change in temperature, it can induce modulation in the phase then the physical properties of the materials also change. This is what we had shown in the previous weeks lecture and this is the proof that it actually occurs.

So, I hope you have understood this concept clearly now. Now, that was macroscopic level. As I said you can also determine the expansion at the microscopic level. So, what you do? You carry out temperature dependent XRD studies. So, you measure the X-ray diffraction pattern as a function of varying temperatures.

Then you determine the lattice parameters let us say a , b and c and volume. Then you plot the lattice parameters or volume as a function of temperature. This is what is shown in figure A and So, if it is a tetragonal cell what will you see? You have $a = b \neq c$. So, what you do? You plot the variation of c parameter and a or b parameter as a function of temperature. You can see that the c parameter is actually decreasing as a function of increasing temperature whereas a or b are increasing as a function of increasing temperature.

But then suddenly at the temperature where you are seeing the phase transformation there is a sharp change in the value. So, you have a change, what type of phase transition it would become? We had seen that at transition temperature, if you have discontinuity, you have discontinuous change in volume, then what is the type of phase transformation? That is first order phase transformation. Hence, these materials clearly are undergoing first order phase transformation and you can also see from the change in volume, you have the change which are quite large and beyond phase transformation you have the positive expansion taking place both in terms of linear or volume because you have transformed from tetragonal to cubic structure. This is what is happening. When you are in the tetragonal phase, you have the off centering of the oxygen atoms and the titanium atom in the middle.

So, you can plot the bond lengths. You can plot this bond length, this bond length or you can plot the bond lengths which are there. So, you can plot titanium oxygen, titanium oxygen 2 that means there are two types of oxygen. This is one type that is of plane, but if titanium and oxygen if they are in the same plane, then they are termed as oxygen 1. So, this is just a nomenclature which is used to differentiate between the oxygen which are above the titanium or they are in the same plane in which titanium is there.

So, you can have titanium bond lengths. you can have lead oxygen bond lengths. So, you can plot and you can clearly see that the dependence of titanium oxygen and average lead oxygen bond lengths are showing negative trend. That means, the expansion is coming in because the atoms are showing less off centering means you are if you are vibrating if you are far away that means you are showing elongation. If you are showing elongation in one

direction that means you are going from the state which is cubic to tetragonal, but if you are vibrating just around the mean position. Then what are you showing that you are a, b and c both are equal and that is the case of cubic lattice and from here you can then conclude that the material is going to transform from tetragonal cell to cubic cell.

When it is moving from NTE to PTE behavior and this is clearly shown that as a function of calcium content you can modulate the properties of this material significantly. Along with that there are class of materials which show nearly zero expansion coefficients. you can have tungsten oxides, you can have zirconium tungstates which actually have negative expansion coefficients, but quite low and you will find that the range of temperature in which zirconium tungstates show negative expansion is huge, it is around 1000 K and you will find it exhibits a cubic structure. So, that the contraction is isotropic whichever direction you want to see the expansion or the contraction is nearly the same. You have seen in silicon carbides it has nearly 0 or even negative thermal expansion coefficients.

You have alumina mellites or aluminum oxide silicon dioxide alloys which show very high negative expansion coefficients making them useful for refractory linings. These materials are being used in aerospace in examples like space mirrors. So, you have a mirror in space during the time sun is shining on the mirror then the temperatures are very high, but when it goes in the region where it is dark then the temperature falls significantly. Now, if the substrate is such that it has expansion as a function of varying temperature what will happen then the alignment of the mirror will change as a function of expansion in the substrate. If the alignment of mirror changes, then if you change the angle of incident by θ the reflected ray will change by 2θ

So, if you have varying angles at which the transmission from earth is reaching this space Then, what will happen? The reflected ray will not reach the control center, but will hit somewhere else and then you are seeing a case where you have loss of signal. So, hence the reflectors, the mirrors they are going to have zero expansion coefficient ceramics on which these mirrors are going to be actually constructed. So, that there is no change in the angle at which the signal is sent back. So, you have reflectors, structural elements and antenna supports where these negative or zero expansion ceramics are used.

You can go to rocket nozzles. Rocket engines generate intense heat during operation, this we have seen from various videos you have seen in pictures, movies. Now, if they expand as a function of heat what will happen? The amount of fuel which is going in the engine will change and then you have the whole thermal management of the system falling apart. So, because more fuel more burning the variation in the heat which is being generated and that is driving your turbines. So, you have to have systems which will not change even if the heat is varying around them.

So, they find lot of expansion in these kinds of applications. If you go to semiconductor industries, obviously you do not want the substrate to change its size when there are variations in the temperature surrounding it. Hence, the negative and zero thermal expansion ceramics are being used in these kinds of applications. You have the same concentrations by which they have become useful in optical devices and lasers. If you look into the MEMS, you will find these zero or negative thermal expansion ceramics actually are being used so that they can minimize the thermal stresses and hence ensure accurate operations. In PCBs, the printed circuit boards, you have electrical connections which are connecting the electronic components using conducting pathways.

Now, if you have these ceramics are being used to print these PCBs, then they will allow better machining with semiconductor components along with reducing the risk of solder joint failures due to thermal cycling's because if you also have expansion and contraction, expansion and contraction as a function of thermal cycling then the solder joints can break, but if there is no expansion the solder joints would be much more stable. You are actually using them in energy and nuclear applications. In nuclear reactors, they are being used as claddings. You are finding that these materials are able to maintain the dimensional stability even at high temperatures and hence they will reduce the risk of deformation or failures. What will happen? It will then prevent fuel swelling and maintain the integrity of the fuel assembly.

They are also being used in neutron absorbers or coatings and insulations, they are used in fire alarms, they are used in systems wherever you want to break or make a circuit as a function of varying temperatures. They are used in solar thermal collectors, they are used in concentrators, in solar concentrators where you can actually get five suns, you can get very high intensity lights. So, they are used in concentrated solar power systems So, that if you have heliostat-based systems then you do not see the change in the mirror or the column of the heliostat even if you go to very high intensity falling on the receivers. Then you have heat exchangers. thermoelectric devices and thermal energy storage systems where these materials are finding their applications.

Hopefully, now you have understood the importance of expansion in solids. It is not always that we want to use the concept of positive thermal expansion in solids to make a useful application out of it, the real and very very lucrative application for these ceramics have come in if they show 0 or negative thermal expansion. We have also shown how to tune the expansion properties in solids. Now, you also know how to measure the expansion coefficient in solids and based on that you can then tune the material which can be used in aerospace to semiconductor industries. These are typical references from which the information were taken and you can read them further to get more information about the topic which was discussed today. Thank you very much.