Biomaterials for Bone Tissue Engineering Applications
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Indian Institute of Science Bangalore
Module 8
Lecture No 37

In this module I will be discussing on that dental glass ceramics materials.

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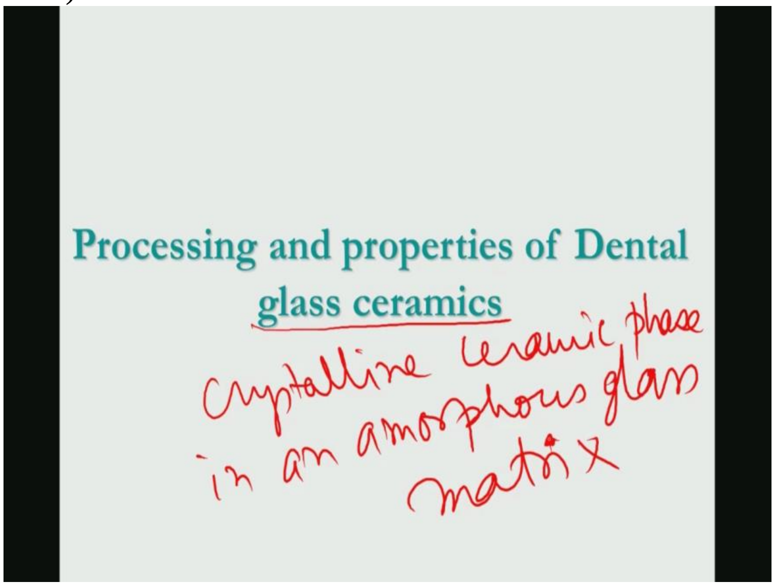

Now this glass ceramics is essentially defined as a materials which contains crystalline ceramic phase in an amorphous glass matrix. Now one of the things that I will be doing in this module is that first I will be briefly introduce to that dental implant systems to start with and then I will discuss rest part of this module only on the processing and properties of some of the machinable glass ceramics.

Now why machinable glass ceramics, that machinable glass ceramics essentially means that because of the presence of certain crystalize morphology in the glass matrix this materials you can get you can get them in the machine to any particular shape using CADCAM based technique like conventional computer aided design and computer aided manufacturing based technique. So this will expand the application of this machinable glass ceramics to a larger extent.

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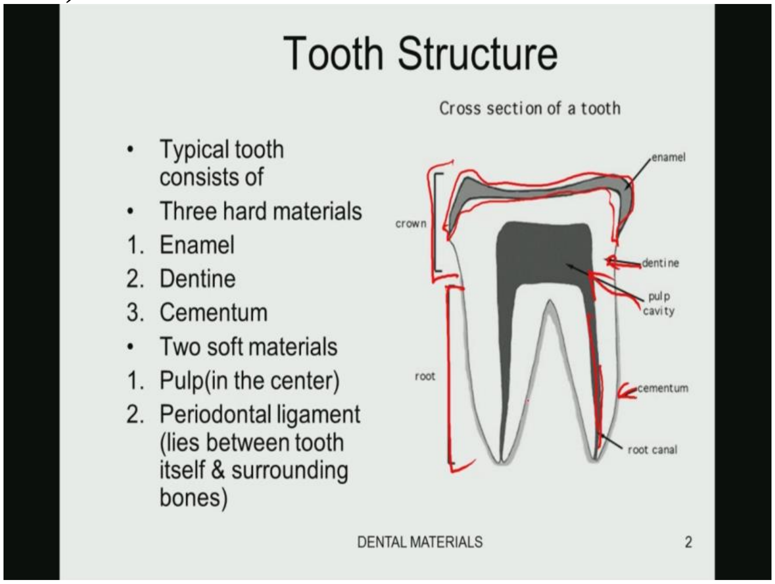

So this a cross section of a tooth so what you see the bottom part is the root of the tooth. Now you have a dentine here and in the top part is the enamel, so enamel is the part where you have harder phase or harder enamel or harder calcium rich phase is there and this top part is totally crowned. So structures you see that the tooth is made of crown and the root part and you have a root canal here. So one of the commonly used clinical therapies or root canal therapy, RCT which is done quite often and you have a cementum here and you have pulp cavity in this part that which is indicated by this arrow.

Now this dental glass ceramics which can be used in this particular case and which will be discussed in this particular module that can be used to make the crown part of the tooth, the root part or the titanium implant essentially that can go inside the damaged tooth part to replace the damaged tooth and the top of it you have to put the crown part.

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So this is the typical ceramic crown as I said that as you can see the ceramic crown why it is so attractive in case of the dental application, simply because ceramic crown has better mechanical properties and also ceramic crown has longer durability and it has good aesthetic appeal as well.

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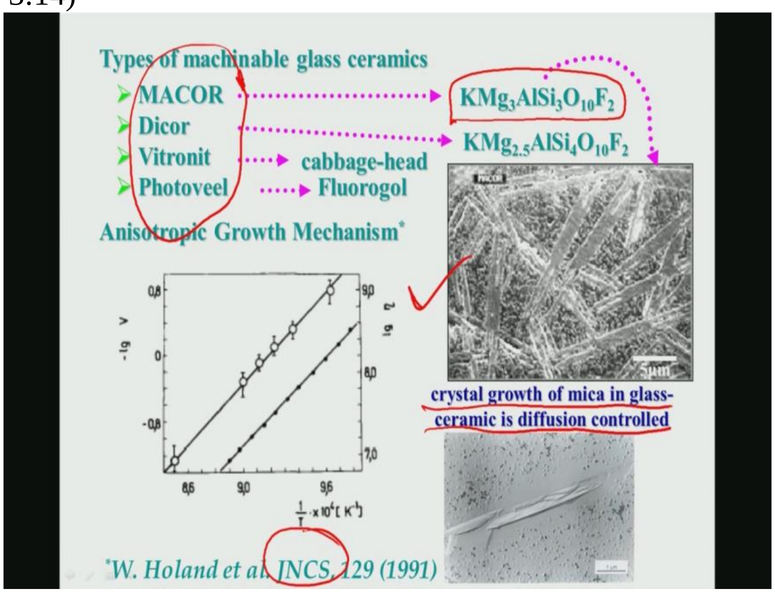

Now this rest of this module I will discuss about this development, processing and properties if that machinable glass ceramic materials. So some of this machinable glass ceramic materials are currently commercially available and that means it is produced by some of the companies internationally and some of the brand and trade names on which this glass ceramics are available these are like macor glass ceramics, dicor glass ceramic, vitronit and Photoveel.

Now all these glass ceramics are characterized or can be distinguished from one another by two things l. One is the composition of the crystals or ceramics phase that is forming and second one the morphology of the crystals or morphology of ceramic crystals that are present in glass matrix. Now why I am stressing too much on the morphology if he ceramic crystals? Because the morphology depends on what are the kind of heat treatment that you are giving to this particular glass matrix.

And because of this heat treatment you can essentially tune the glass ceramic composition that is being nucleated in the class matrix and also that their morphology that is also you can have some control. So this is the SEM image just to show crystal growth of mica glass ceramics, mica in the glass ceramics diffusion control and this is published way back in 1991, almost 25 years ago in journal of non crystalline solids.

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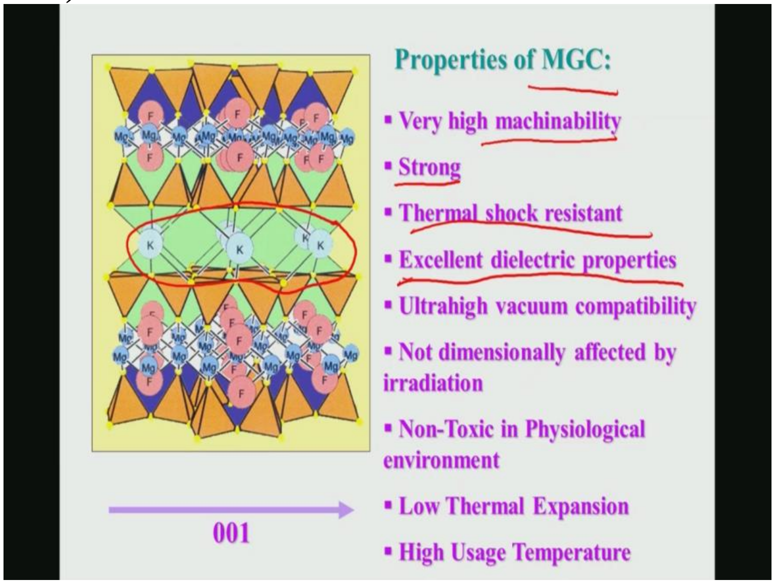

Now what are the properties of mica based glass ceramics, that is good machinability, they are strong , there is thermal shock resistance and these are good excellent dielectric properties and so on. Now as I said that it has a very characteristics morphology and you can see that is the network of potassium, florins, magnesium, ions they are present in a particular Tetrahedral arrangement as well as very characteristics crystal or morphological features when this crystals are viewed along 001 directions.

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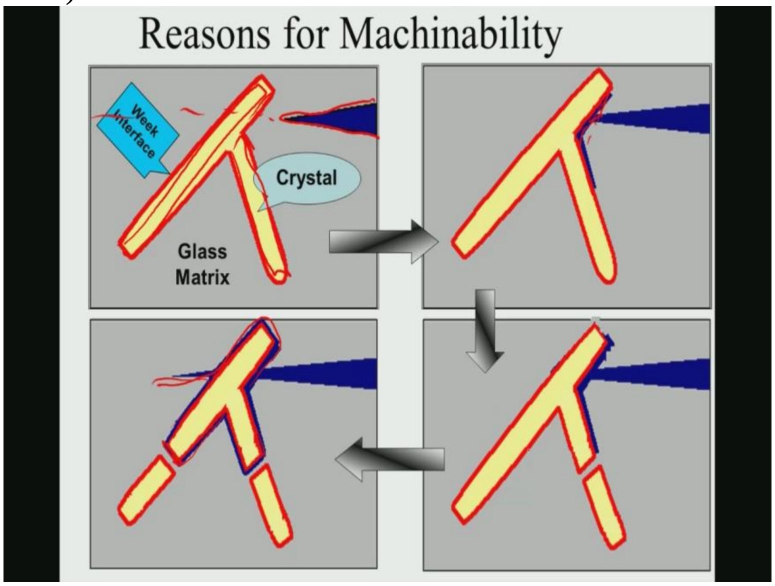

Now what is the reason for this machinability? Now suppose you have a straw like crystals in the materials, this is like straw like crystals in the materials, and this straw like crystals are essentially anisotropic crystals. Now the moment a crack comes, now crack cannot go straight away to the other surface to the other face of the material. And these if you have a very weak interface them when a crack comes, as it has been shown here, crack now can be branched or they can be planted.

Now when it comes and planted then it can go to the other surface only after deflection through the boundary of this anisotropic crystals. And this anisotropic crystals, since it is also brittle because it is ceramic, they can break or they can fracture at any specific part of the crystal and in a very random manner and then after that this crack can find its original path, because crack always has a tendency to trace back it is original path of propagation so that it continues to propagate in the unaltered direction through the glass matrix.

So this is what has been shown here in a very schematic manner. So the more is the resistance to crack propagation through this specific crystal arrangements in this class matrix, the more or better will be the machinability. Now if a material can be fractured very easily by the propagation of the crack you cannot give it a particular shape to this material, simply because you do not have any control over the way this crack will propagate through this micro structure.

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Now to substantiate my statement what I have made like few minutes ago, that indeed it is possible through heat treatment procedure that you can have different crystal morphology, they are distributed in different manner in this glass ceramic materials and this has been shown here, this is in case of Fluorophlogopite based mica based glass ceramics, the first stage that has been shown that is the phase separation. Phase separation means that is prior to the nucleation of the crystals.

Now when you heat treat this material at 640-750 degree Celsius you form the contrite phase that it has a different structural features and then which changes to Norbegite when it is in the when it is heat treated to 750-850 degree Celsius. Finally when you heat it at in the temperature range of 850- 1100 degree Celsius you get more equilibrium fluro flugoparidephase with a characteristic straw shaped crystal morphology here. And what is equilibrium composition here, you get klsi2o6 plus magnesium silicate and magnesium fluoride based composites.

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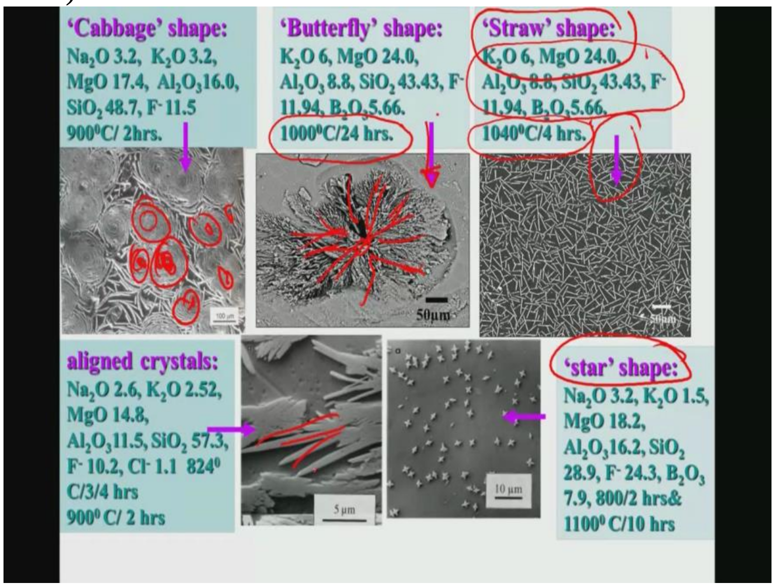

Now in one of our recent work we have we have observed that depending on what is the composition of base glass you can indeed actually have a control on this morphology of this glass ceramics. So this straw shaped morphology was obtained from the same glass composition which is heat treated at 1040 degree Celsius for four hours. But if you do the heat treatment for longer time period for the same glass at 1000 degree Celsius for 24 hours we see what we call butterfly shaped.

So this is the nucleation point and then all the crystals they are kind of very lovely and in very unique manner they are growing in different directions giving it butterfly shaped. Another shape which is also reported in literature but for a different class matrix what they call cabbage shaped crystal. Now this cabbage shaped crystals what you see is certainly there are lot of concentric rings like onion.

And this concentric rings it is forms at position in a very dense manner in a glass matrix and which is indeed different in morphology compared to a strong shaped crystals. Then also people have reported star shaped crystals like na2o, 3.2k2 and all these things and also aligned crystals like you can see this very well aligned manner these crystals are formed in this particular material.

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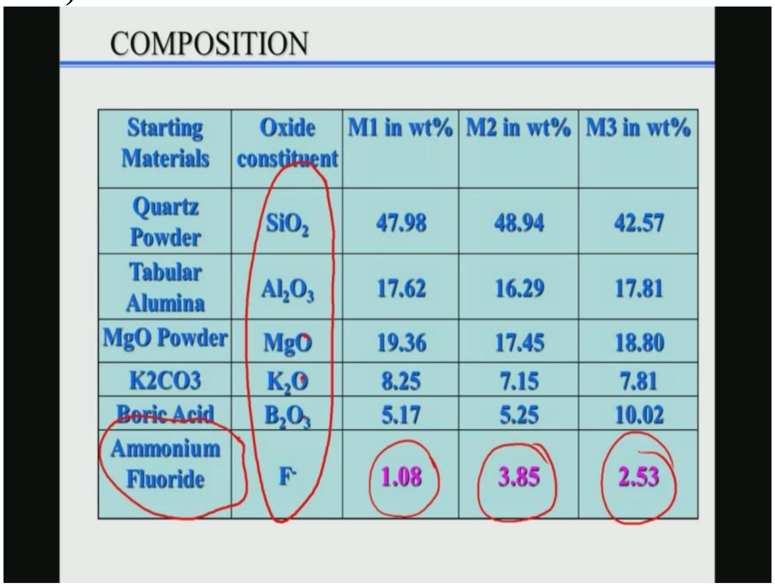

COMPOSITION

Starting Materials	Oxide constituent	M1 in wt%	M2 in wt%	M3 in wt%
Quartz Powder	SiO_2	47.98	48.94	42.57
Tabular Alumina	Al_2O_3	17.62	16.29	17.81
MgO Powder	MgO	19.36	17.45	18.80
K2CO3	K_2O	8.25	7.15	7.81
Boric Acid	B_2O_3	5.17	5.25	10.02
Ammonium Fluoride	F^-	1.08	3.85	2.53

Now coming to that this case study which is again based on a published work and this is based on the tented thesis work of two of my former student form IIT Kanpur. One is Athiyar Mole and one is Shiban Rai. And this material is based on sio2l2o3 magnesium oxide k2ob2o3 and little bit of fluorine also being incorporated through the of use of ammonia fluoride as a precursor. So essentially all these powders as well as their precursors are added in a specific ratio in a different glass composition just to vary the fluorine content and fluorine content is varied over 1 to 4, percent.

In this narrow window we are seeing that how fluorine content can give rise to other glass ceramic materials with different morphology a and b with different properties both physical and bio compatibility properties. I repeat once again this is a silica based glass but other elements or this is silica based multi components glass materials but with other composition they are mostly oxide based, like alumina, magnesium oxide k2 and b2o3 and the fluorine has been incorporated in this class ceramic through the use of the aluminum, ammonium fluoride a s a precursor.

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COMPOSITION

Starting Materials	Oxide constituent	M1 in wt%	M2 in wt%	M3 in wt%
Quartz Powder	SiO_2	47.98	48.94	42.57
Tabular Alumina	Al_2O_3	17.62	16.29	17.81
MgO Powder	MgO	19.36	17.45	18.80
K2CO3	K_2O	8.25	7.15	7.81
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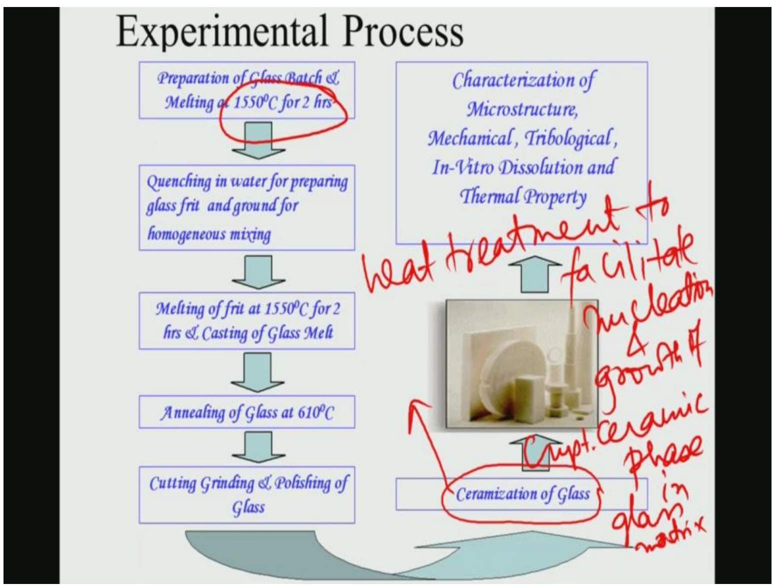

Now how this glass materials are being processed that is very important to note here. So essentially all these oxides initially. After they are mixed using the ball milling technique then they are simply melted at a temperature of 1550 degrees for two hours in a conventional sintering furnace, then once it is melted, this melting experiment or melting is to be done in a platinum crucible. Why platinum crucible, if you do it in alumina, alumina can sustain 1600 very easily, but then there will be pick up of the alumina from the crucible itself in the glass matrix, so that actual balance of the different oxides which you have done initially at the design of the glass composition itself, that will be disturbed.

In other words what I am trying to say is that, if you use alumina crucibles to make this particular glass ceramic composition or glass composition, what will happen? You have alumina in the base glass right? Now if this composition is melted in alumina crucibles then what will happen, there will be additional alumina pick up form the alumina crucible so that this targeted composition or this initial composition will not be same the way you are showing in the table, so it will be disturbed.

So in order to avoid this kind of pick up or contamination from the crucible, the platinum crucible which is very inert and which can also sustain high temperature that is to be used for the glass melting and that is used worldwide in most of laboratories who prepares the glass. Then after that you just simply quench the glass in water and to prepare the glass fret, glass fret means the chunks of glass that will get. Then you ground, then you grind it and then you do it additional melting.

Why this additional melting is required? Because just to observe and let me emphasize it again it is a multi component oxide based glass. So it has not only silica but alumina, magnesia, potassium oxide and boric acid or boron oxide is also there. And their amount is not negligible, it is large amount. This homogenous mixing of all these oxides requires not only one melting but multiple melting so that these materials are very homogeneously mixed.

After you do this things then you cast this glass melt in a usable form and after that you anneal this glass at different temperature like 610 degree Celsius. You do this things and after that you do ceramization of the glass. What is ceramization? Ceramization is the heat treatment procedure which will enable the nucleation and growth of the ceramic phase in the glass matrix. So ceramization is essentially a heat treatment to facilitate nucleation and growth of ceramic phase of crystalline ceramic phase in the glass matrix.

And ceramization process actually takes place at a temperature much lower than the melting temperature of the glass but usually high enough so that there is enough driving force for the nucleation and growth of the crystalize ceramic is there in the glass matrix.

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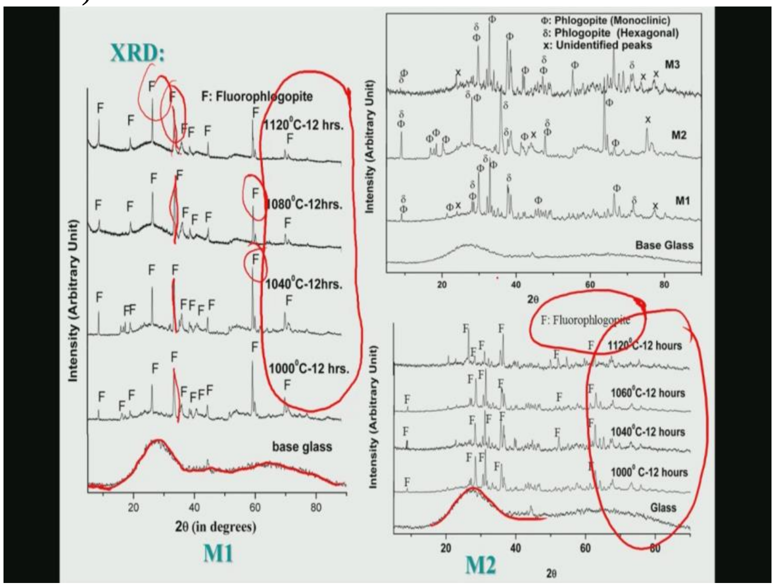

Now to illustrate further that ceramization process in this particular case was carried out at different temperature of 1000 degree Celsius to 1020 degree Celsius by holding them, by holding the glass at this different temperature for 12 hours. Now depending on what is the temperature that you are holding it for 12 hours, what you see that initially the glass has a very large hump and this hump essentially is a characteristics of any amorphous material.

Like it does not have a very sharp peak but rather a broad hump kind of thing. And this shows that (())(15:13) glass peak. Now when you crystallize them or ceramize them at 1000 degree Celsius, you see that all this characteristics Fluorophlogopite peak which is rather sharp and that it shows that crystalline Fluorophlogopite that is starts appearing and with higher and higher temperature holding at 1040 or 1080 to 1120 this peak, their intensity increases to many extent.

And also their sharpness of the peak also increases. That means they are becoming more and more crystalized. So this is in the case if m1 glasscomposition . In case of m2 glass composition also we have seen that similar fluro flugoparidebased so it is monophasic glass ceramic materials. Initially base glass is amorphous and then all other characteristics of fluro Fluorophlogopite peaks are appear at higher sintering temperature.

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Now in terms of morphology what we see that this mica straw like crystals they are forming not only in one direction but also in different directions depending on whether this materials are crystallized or ceramized at 1000 degree Celsius for 24, hours.

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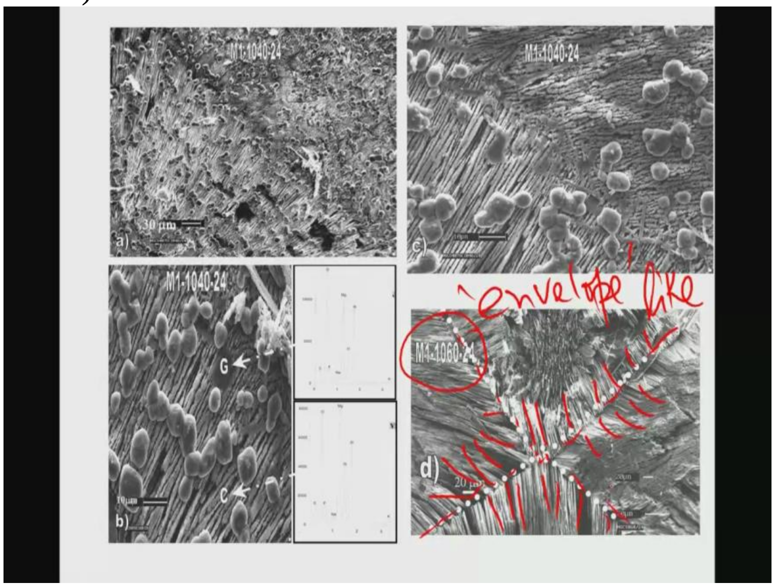

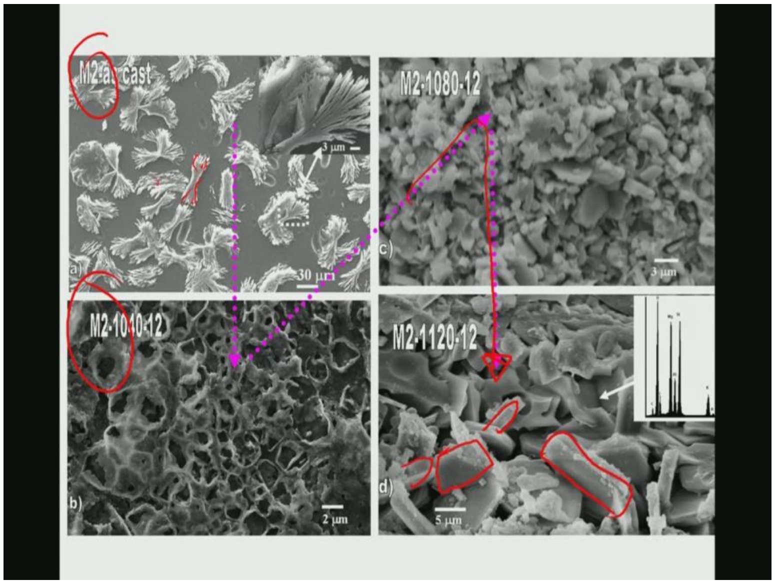

Interesting enough when this materials were ceramized at 24 hours at 1060 degree Celsius what we what I describe this morphology as like envelop like crystals. This like you know postal envelope, so it is like envelope like crystals. And this crystals essentially has four different domain and each domain the straw like crystals are oriented in a particular orientation and this orientation differs and this orientation there is a clear transition at the domain boundary which is shown here in the dotted line.

So this kind of morphology is indeed different from what I have described in the earlier slides where I have shown cabbage shaped crystalline or star shaped morphology compared to that this is indeed different. The other interesting thing that you notice here this stacking od this crystalize or rod shaped morphology, it is indeed very dense. So it is not like in the same way that you have seen that which are dispersed in the micro structure but it is very dense straw like morphology but in a very dense manner.

And this kind of dense arrangement of this crystals in the glass matrix would essentially give rise to better mechanical properties which we will see in some of the next slides. But this morphology is certainly sensitive to the composition of the base glass the way you are choosing like you go from m1 to m2 and m2 ascus means without ceramization. So without ceramization you see that this material, this crystals also have different morphology.

And then once you start crystalizing then you see that different type of crystal formation but these crystals does not have any specific morphology or very regular morphology the way you see or the way you have seen in the earlier slides.

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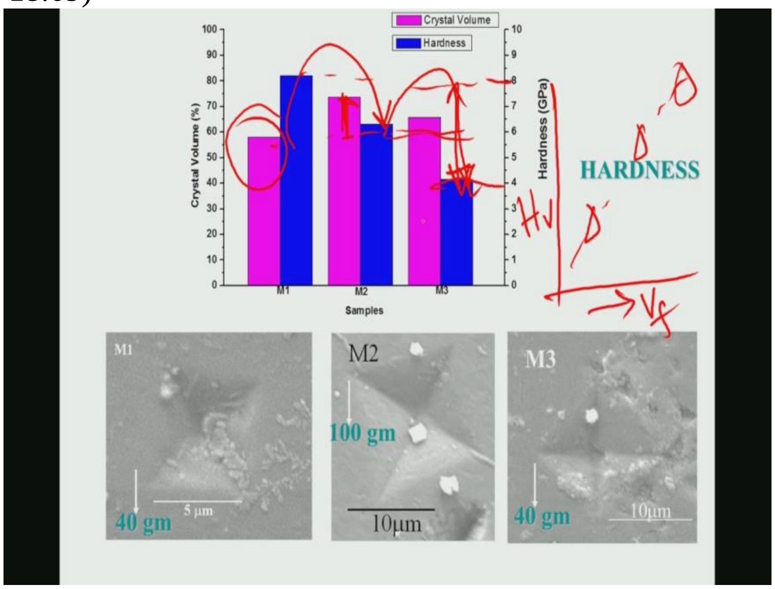

Now in terms of hardness of this materials, now this blue ones is the hardness. What you see this materials has hardness of 8 giga Pascal. Just to give you the relevance of this value of 8 giga Pascal, the steel material which is when hardened in the fully martensite conditions, they have the hardness of 7 gigaPascal. Now compared to fully hardened steel this glass ceramic has almost equal or identical hardness of 8 gigaPascal which is extremely hard and this extremely high hardness can be attributed to the specific crystal morphology that I have described to you a few minutes back and which I described using envelope like crystal.

So those type of characteristics crystal morphology is helpful to get that hardness value as so high more than 7 giga Pascal. And what is the crystal volume fraction? That is up to 60 percent volume percent of the crystal which is also indeed very large number. So essentially by varying the base glass composition thecrystal volume fraction varies in the range of 60-70 percent and hardness value varies in the range of 4-8 gigaPascal.

So another interesting thing is that normally one can assume that if you plot the volume fraction of crystal volume fraction of the ceramic phase in the glass matrix and if you plot the hardness on the y axis, normally one would expect larger the volume fraction of the crystals more is the hardness value. But that is not observed, this kind of trend is not observed here simply because here the morphology changes, as you go from m1 to m2 as I have shown you before and you go to m2 to m3 the morphology, crystal morphology changes.

And because of that change in crystal morphology that any kind of systematic trend with the increase in the volume fraction of the crystals to an increase in the hardness, that could not be realized in the present case.

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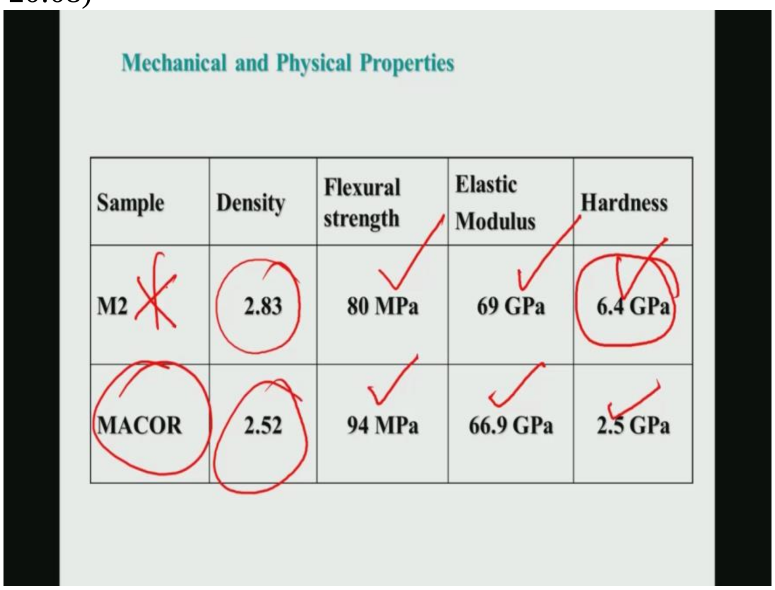

Sample	Density	Flexural strength	Elastic Modulus	Hardness
M2	2.83	80 MPa	69 GPa	6.4 GPa
MACOR	2.52	94 MPa	66.9 GPa	2.5 GPa

So this is that some of the other properties, and just a comparison with the commercial micro based glass ceramics, so that density of our glass material is 2.8, micro glass is 2.5, flexural strength was 80, macor was 94 mpa, elastic modulus 69, here it is 67 gigaPascal hardness was 6.4, higher the hardness better is the wire resistance, and better is the durability of this material. So our material that which was an experimental material, I put a star, and why I put a star because that really has much better properties than some, and then one of the commercially available dental glass ceramic.

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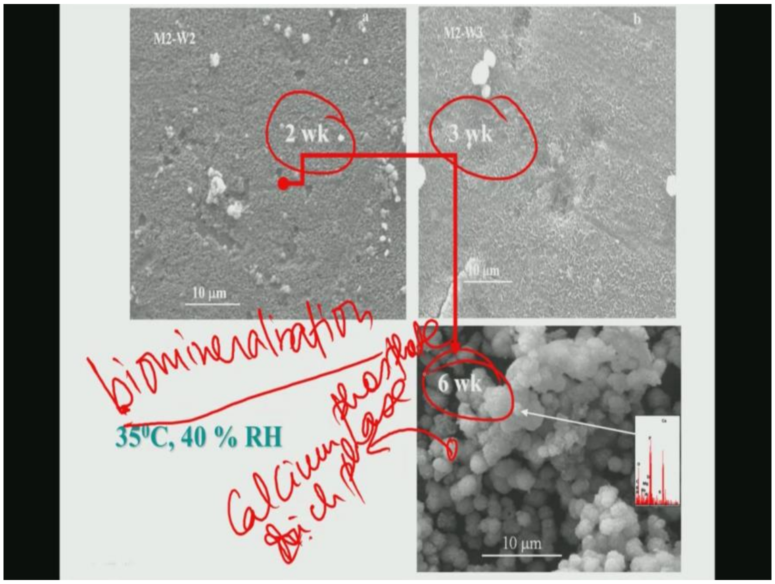
in vitro property

COMPOSITION

Starting Materials	Oxide constituent	M1 in wt%	M2 in wt%	M3 in wt%
Quartz Powder	SiO_2	47.98	48.94	42.57
Tabular Alumina	Al_2O_3	17.62	16.29	17.81
MgO Powder	MgO	19.36	17.45	18.80
K2CO3	K_2O	8.25	7.15	7.81
Boric Acid	B_2O_3	5.17	5.25	10.02
Ammonium Fluoride	F^-	1.08	3.85	2.53



Now coming to this in vitro properties, now this material does not contain any hydroxyapatite, this material does not contain any calcium ox, I think it contains calcium oxide, if I go back to this one, it does not contain any calcium oxide. So if this this glass ceramic material does not have any precursor material which can facilitate the formation of the, hydroxyapatite formation in the in vitro. But when this material is dissolved or this material are incubated in a simulated body fluid with some of the precursor solution, what we have seen interestingly that these nodules are essentially calcium phosphate. This material is calcium phosphate rich phase.

Another interesting things that we have seen is this calcium phosphate rich, lobular shaped, this is called, the process is called bio mineralization. Why it is called bio mineralization? It is called bio mineralization simply because that it does not have any calcium phosphate phase here but it produces calcium phosphate nodules when it is dissolved in vitro in a simulated body fluid solution and these nodules do not appear immediately after the incubation, but when you incubate this material for 2 weeks then 3 weeks, up to 6 weeks then mineralized rich layer forms, mineral rich later forms.

So which essentially shows that this material can make good biological bind with the osseous structure, with the tissue structure, why because you are natural bone or hard tissue is also mineralized tissue right? And so if if you have mineralized tissue when they will see on a material surface where there is a mineralized later formation automatically there will be a better compatibility with the natural osseous structure.

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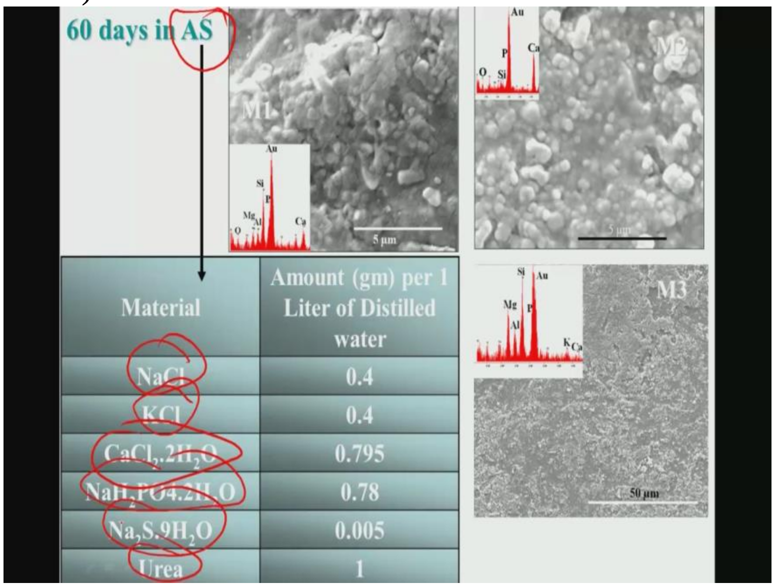

So I hope I have emphasized this point enough so that you understand that it is possible for a material without even containing calcium oxide or some of the precursor of the calcium phosphate rich, but they can indeed form this calcium oxide, calcium hydroxyapatite formation when they are dissolved in artificial saliva for example. Now artificial saliva has a typical composition of sodium chloride, it is sodium chloride, calcium chloride, potassium chloride, nah2po4, na2s and some urea.

So artificial saliva essentially stimulates that oral micro environment that a dental crown or dental material is expected to experience during application, so that is why that artificial saliva is to be used for all in vitro studies related to the bio mineralization of this material. Ok.

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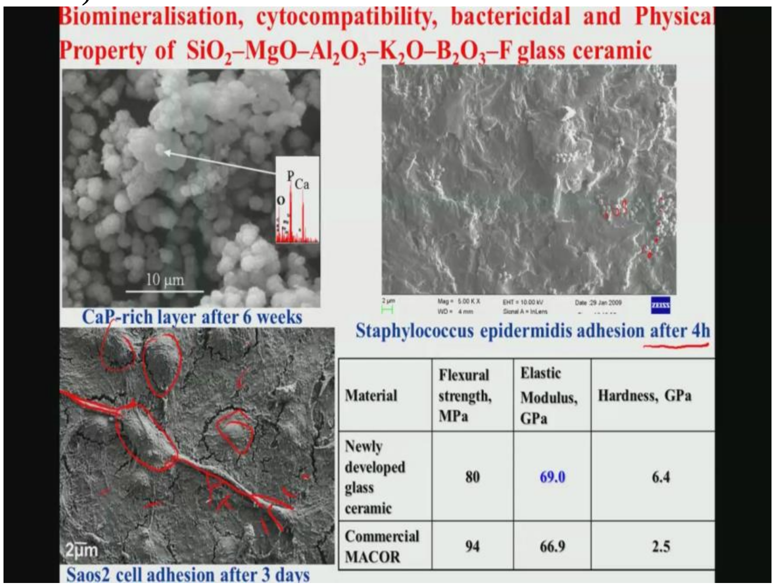

Now coming to the some of that cell study like in vitro, cyto compatibility or bactericidal studies, this is certain neat results that we have obtained and quiet encouraging results so anti microbial properties we have studied using staphylococcus epidermidis as one of the bacterial strength that is gram positive and their addition on the glass ceramic were tested after 4 hours of growing them in this luria broth growth medium. Now after 4 hours you do see some staphylococcus oreous bacteria, but when you compare with that of the control, with bacterial addition of the control, this number of bacteria is certainly less.

Another thing that we have noticed that when you have grown curcuma, osteo curcuma cells that is that one of the osteoblast cells, it shows a very flattened kind of morphology and also it shows a very long filopodial extension and there is a number of this flattened cell morphology, you can see here and also there are indications that is the extra cellular matrix like layer formation when these cells have reached the confluent state.

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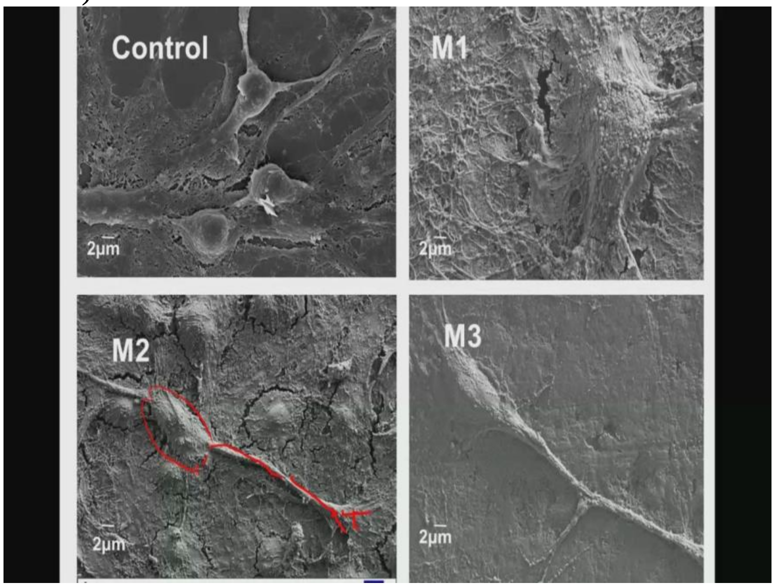

This is more clear here. And you can see here that how this filopodial external cellular breach formation they are forming on this material.

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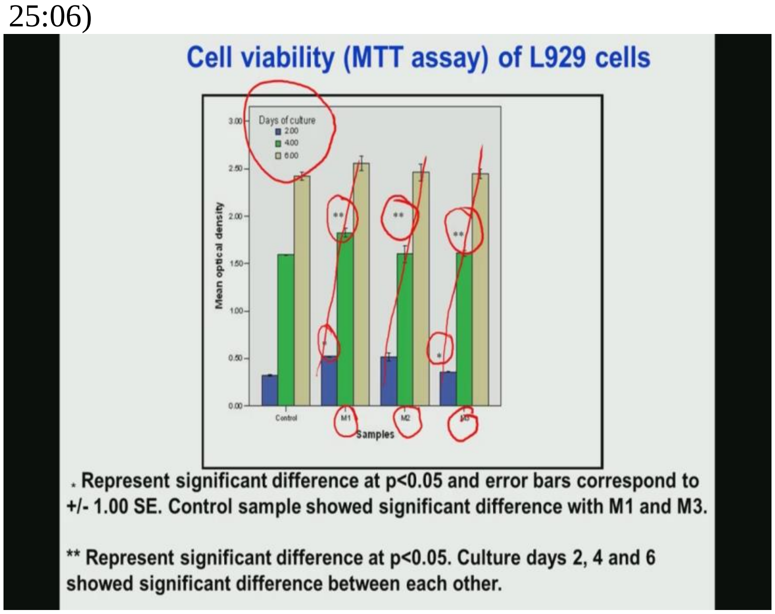

Now in terms of the mtt assay of that l929 mouse fibroblasts cells, these are the three composition we have tested, one is m1, one is m2, and one is m3. And their days of culture is 2, days, 4, days, and 6 days. Now what you notice here, in the control m1, m2 and m3 these three type of material, that l929 cells, they grow because that there is a systematic increase in the entity of optical density values that means that larger the optical density values more is the number of myto quantity viable cells. So when cell grows in an interpreted manner, in a very linear manner that means this glass ceramic material can be used as cell growth substrate also. And there are certain statistical significance aspect has been highlighted in this slide, and essentially it shows that with respect to control at different times points in culture how this glass ceramic material they have a different statistically significant increase in the optical density.

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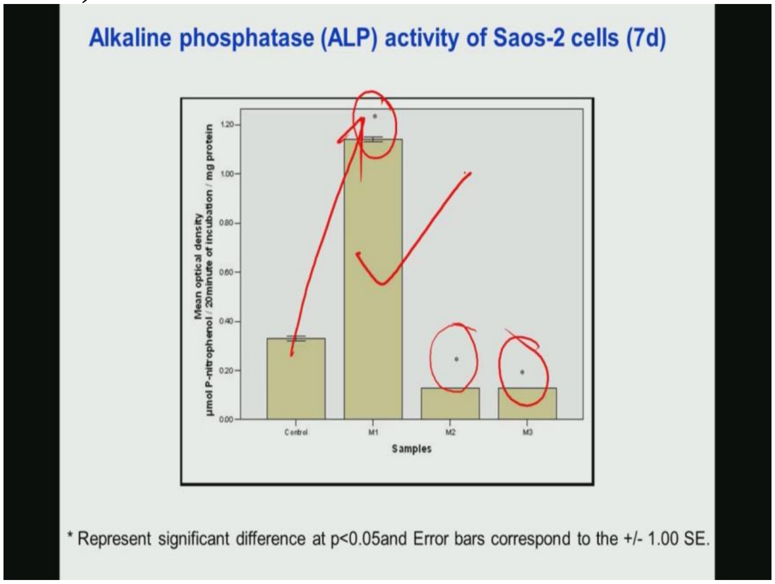

Now alkaline phosphorus expression or activity has also been quantified on this material using curcuma osteo curcuma so that is the early differentiation marker of the bone cells. And what you see that lp expression is much higher compared to the controlled here in m1 glass and m2 andm3 they do not support this kind of differentiation of bone cells essentially that m1 is better in terms of cell level compatibility property is concerned.

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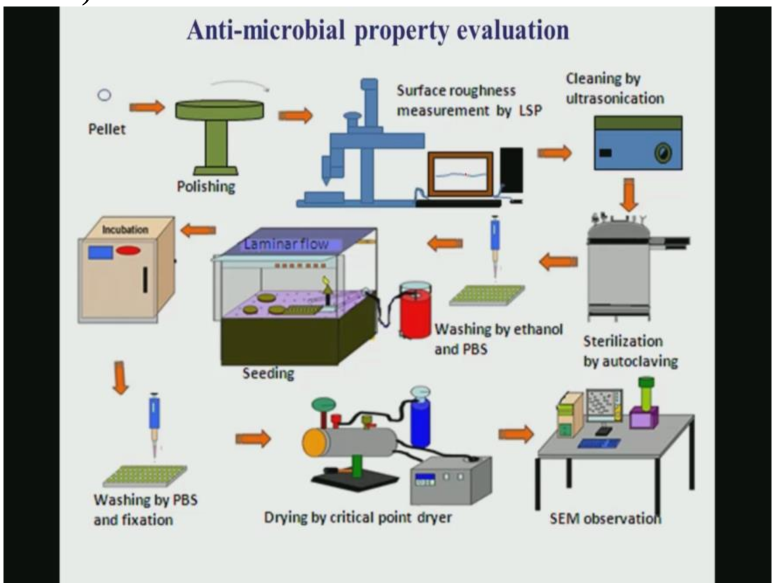

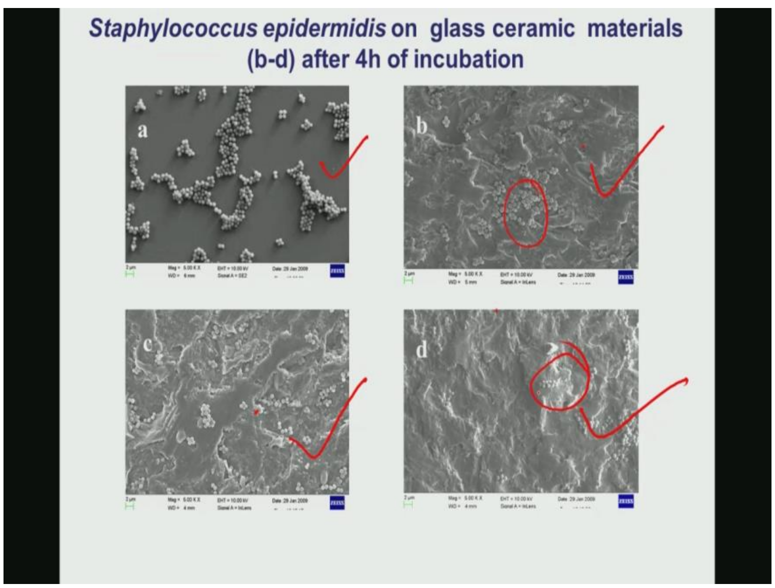

Now little bit more details of the anti microbial study, so you have the control here, this is the control. This is the bacterial addition on the controlled sample that is (())(26:50) plastic. This is that m1, this is m2, and this is m3. Now with respect to control certainly you see that m1, m2 and m3, there is less number of bacterias that adhered, the second thing that you notice m2 and m3,m1 and m3, there is a significantly more compared to the control sample.

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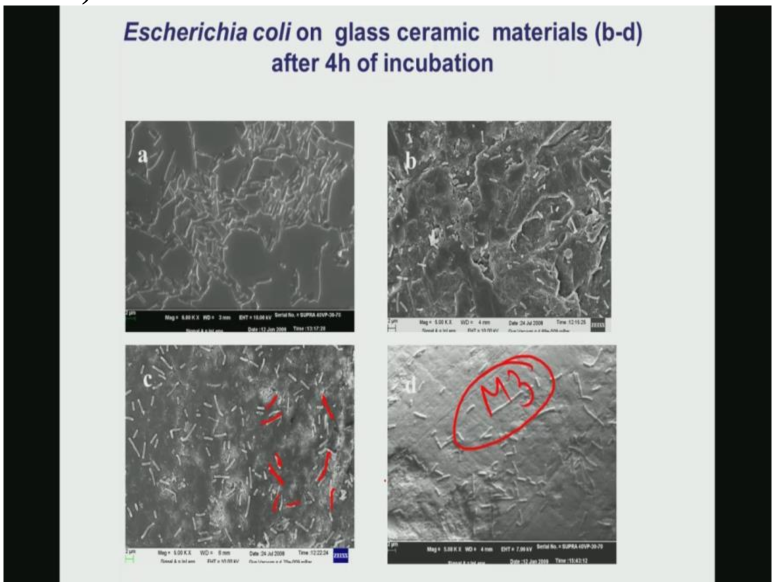

As I said in earlier modules also that in order to establish anti bacterial property one has to use the two bacterial strengths and indeed we have used two bacterial strength one is the staphylococcus oreous and this is the one escherichia coli. And escherichia coli also we have seen less number of bacteria which are growing or which adhered in the material substrate like m1 and m2 and m3 and particularly m3 is even less number of bacteria are present.

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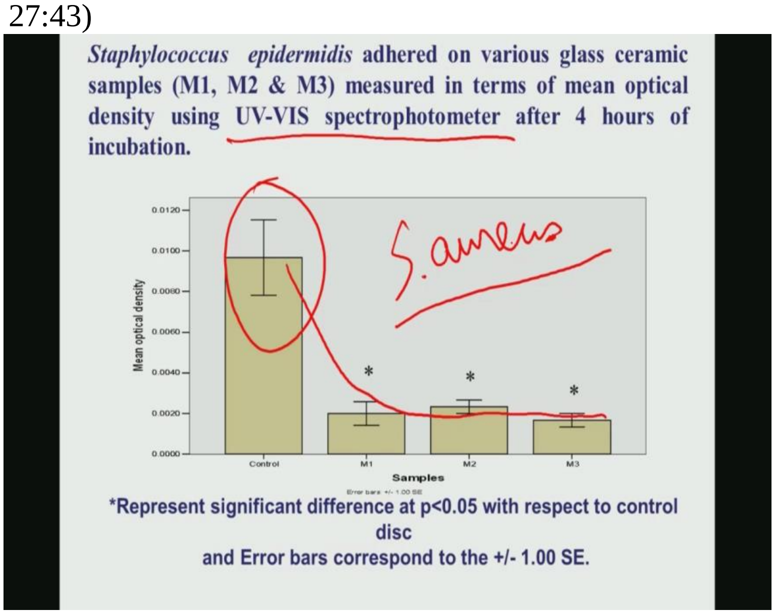

This quantification is done using UV visible spectrophotometer, and then what you see here, this is the reading with respect to control. Now compared to control m1, m2, m3 there is indeed significant decrease in the optical density values so therefore they show that s oreous bacteria, s oreous bacteria their growth is inhibited to a large extent on this m1 m2 m3 glass ceramic. So they not only have anti bacterial property but they also can be used as a good cell growth substrate to facilitate cell viability and cell survival on this material.

So this brings us to the end of this dental glass ceramic materials. So so far I have covered this different case studies just to highlight how to develop material for different application including dental material application. How to design that specific material composition, how to process this different materials? And particularly I have emphasized that in case of dental glass ceramics that this combination of the glass melting, casting and heat treatment that is indeed different from the rest of the ceramic processing which extensively involve either conventional sintering or spark plasma sintering or other advance sintering technique.

So this glass melting is also kind of unique in the sense that one time melting is not enough, you have to do multiple melting to ensure homogeneous mixing of the multi components oxides or multi component phases in the glass matrix before one can start the ceramizing treatment. Because ceramizing is one of the treatment which is to be conducted in a uniformly uniformly melted glass composition so that you have that equal potential sides for the nucleation of the ceramic phase.

If there is composition in homogeneity in the base glass itself so therefore chances of nucleation of the ceramics phase will be different depending on whether there is a composition or segregation. So you have to rule out any composition heterogeneity in your base glass matrix before you start the ceramization and thereby you ensure that base glass has equal potential to act as a substrate to nucleate the ceramic phase on this material when they will experience the heat treatment.

And once this crystalline phases are distributed uniformly in this material then you will have better chances of uniform ceramic phases being crystalized and growing and the glass matrix uniformly. And once you have this total crystalline ceramic phase on this material and in a very dense manner, then this materials is a expected to have better mechanical properties also, as well as their in vitro or in vivo bio compatibility.

Another thing is that I have emphasized in the dental glass ceramics that it is not important to have hydroxyapatite based, hydroxyapatite phase or any precursor phase in the material to induce the bio mineralization in the in vitro. Bio mineralization means, I repeat, that is the ability of material to form calcium phosphate rich layer when they are incubated in a physiologically physiological environment, be it simulated body fluids or be it artificial saliva. In those kind of physiological environment if a material is incubated for a sufficiently longer time period whether the material has the ability to show that it indeed can support the calcium phosphate rich later formation.

Here in the case of glass ceramics that we have discussed in this module, I have clearly shown when this material is incubated in artificial saliva for sufficiently longer time period up to 6 weeks in artificial saliva, it can show very distinct calcium phosphate rich globules or very spherical globules in a dense manner it forms very clearly on the surface and once this mineralized layer forms it has a greater acceptability in the body environment simply because that although this is not that hydroxyapatite rich glass but it has that hydroxyapatite rich surface phase. And having that hydroxyapatite surface phase it will help in the Osseo integration because your hard tissue or bone natural tissue also is mineralized tissue. That means it also contains hydroxyapatite phase. So therefore in order to have, because they have a compositional similarity they will have better integration in that osseous system. Thank you.