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LOW TEMPERATURE SYNTHESIS OF ZR02-TI02 AND SI02 GLASS

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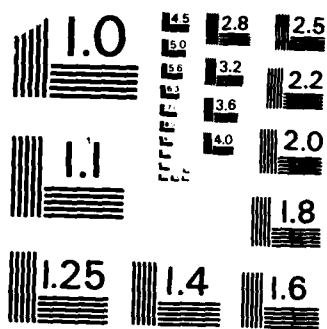
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 $Ti(OC_4H_9)_4$ AND $Si(OC_2H_5)_4$

by

Hou Li-song, Zhu Cong-shan, Xie Juan-Juan



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26 November 1986

MICROFICHE NR: FTD-86-C-002416

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English pages: 15

Source: Guisuanyan Xuebao, Vol. 11, Nr. 4,
December 1983, pp. 422-429

Country of origin: China

Translated by: FLS, INC.

F33657-85-D-2079

Requester: FTD/TQTD

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LOW TEMPERATURE SYNTHESIS OF ZrO_2 - TiO_2 AND SiO_2 GLASS FROM $Zr(NO_3)_4$, $Ti(OC_4H_9)_4$
AND $Si(OC_2H_5)_4$ *

Hou Li-song Zhu Cong-shan Xie Juan-juan**

Journal of the Chinese Silicate Society, Vol.11, No. 4, Dec. 1983

→ Using $Zr(NO_3)_4 \cdot 5H_2O$ as one of the starting materials, glasses in the system ZrO_2 - TiO_2 - SiO_2 were prepared by the sol-gel method. The influence of various factors on the gelling properties of the system, the variation of viscosity with time of the reaction system, the different environmental conditions on the unity of gel mass and the effect of heat treatment conditions on the final results have been studied in detail. In order to investigate the change of dry gels during heat treatment, DTA and IR absorption spectroscopy analysis were also made. On the basis of the above studies, small transparent glass pieces were obtained, and some problems were discussed, such as the method of adding water into the reaction system and the function of $Zr^{(4+)}$ ion in the glass, etc. (China Translation)

* Received Sept.7, 1982

** Xie Juan-juan is a 1982 graduate of the Shanghai Technological Science University. Comrade Jiang Zhong-hong checked and approved this text and also brought forth suggestions. We sincerely thank each of them.

FORWARD

The low temperature synthesis of glass oxide has many advantages¹⁾. It is especially suitable towards the preparation of the glass group possessing a high melting point, or in the glass group which under high temperatures easily split and crystalize.

With ZrO_2 and TiO_2 silicate glass there is found a good anti-alkalinity²⁾ and a very low heat expanding coefficient³⁾, but because of the very high melting points of ZrO_2 and TiO_2 ⁴⁾, using traditional melting processes for these types of glass is difficult. Consequently, in recent years many people have conducted studies on the low temperature synthesis of TiO_2-SiO_2 ⁵⁾, ZrO_2-SiO_2 ⁶⁾ glass, and have produced membrane⁷⁾ fiber⁸⁾ or small glass pieces⁹⁾. As for the synthetic glasses in the $ZrO_2-TiO_2-SiO_2$ system, to date we have only seen the works of Masayuki Nogame and Yoshiro Moriya¹⁰⁾. They have produced non-crystalline membranes, researched the membrane refracting power and anti-alkalinity stability, along with the glass compositional change.

Low temperature synthesis of glass oxides for the most part used various ester types and metal alcoholates as starting materials. Recently, the use of soluble inorganic salts as starting materials has also been studied. T. Havaishi¹¹⁾, etc., attempted to synthesize $CaO-SiO_2$ glass using $Ca(NO_3)_2$ and $Si(OC_2H_5)_4$ as starting materials and only created a very low density glass powder. M. Yamane¹²⁾ used $Sr(NO_3)_2$ and $Si(OC_2H_5)_4$ as starting materials in the synthesis of small pieces of $SrO-SiO_2$ glass. When Sumio Sakuhana¹³⁾ used $Zr(n-C_3H_7O)_4$ as a starting material to prepare ZrO_2-SiO_2 and $Na_2O-ZrO_2-SiO_2$ glass fiber, he discovered $Zr(n-C_2H_5O)_4$ is greatly volatile. Currently there is still no domestic supply of zirconium acid ester reagent. We use $Zr(NO_3)_4$

as one of the starting materials in the study of the low temperature synthesis of $ZrO_2-TiO_2-SiO_2$ glass. The method of adding water, the ratio of solvents to be used, the usefulness and varieties of catalytic promoters, the influence of humidity conditions, etc., on the gelling period, the variation of viscosity with time of the reaction system, and the different environmental conditions on the unity of gel mass have all been studied in detail. DTA analysis of dry gels and IR absorption spectrophotometry of dry gels under heat treatment at different temperatures over time were both conducted. Finally, experimental parameters were chosen, hydrolysis using separate steps was employed, and the slowly rising and falling temperature heat treatment method was used in an O_2 atmosphere. Measurable small transparent glass pieces were obtained (Fig.1), refracting power was determined, and using theoretically calculated values comparisons were made.

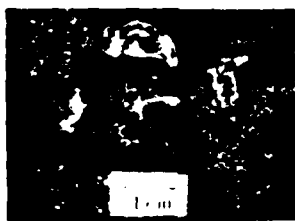


Fig.1 Photograph of glass
 $5ZrO_2 \cdot 20TiO_2 \cdot 75SiO_2$ (made
by sol-gel method)

PREPARATION

1) Materials and Procedure

The pure chemicals used are zirconium nitrate [$Zr(NO_3)_4 \cdot 5H_2O$], ethyl silicate and butyl titanate. Anhydrous ethanol is used as a solvent. Using a magnetically stirred reflux reactor the synthesis reaction was carried out.

2) Steps

The six different ZrO_2 content systems researched in this work are arranged in Table 4. The complete preparation procedure is as illustrated in Fig. 2.

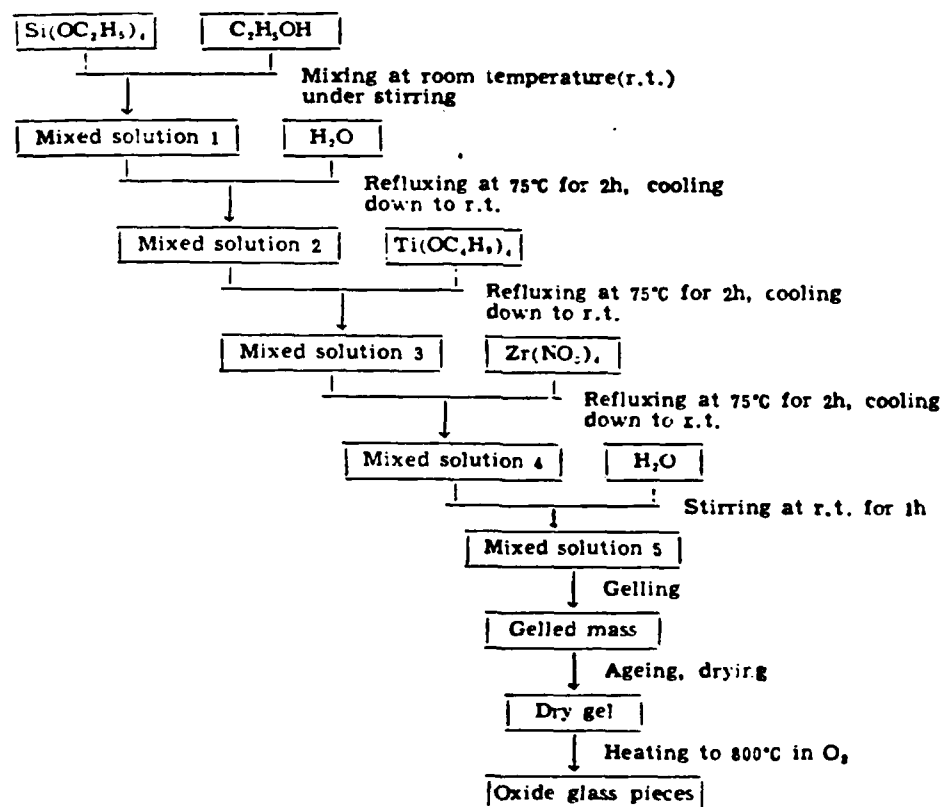


Fig. 2 Schematic illustration of the preparation procedure

3) Measuring Gelling, Dry Gels and Glass

3.1 Determination of Gelling Time

Create a mixed solution in the reaction system whose viscosity constantly increases, then finally changes into a gel mass completely void of any fluidity. The period of time starting when the container can be tilted 45° , at which angle the gel's surface does not move, is fixed as the gelling time.

3.2 Variation of Viscosity in the Reaction System

After setting the mixed solution for seventeen hours, measure its viscosity on a rotating viscosity gauge each consecutive fixed time period. Make a $\lg\eta-t$ curve.

3.3 DTA Analysis

Grind the dry gel into powder, use a QT-2 type Shimadzu thermal analyzer to determine the DTA curve. The rise in temperature speed is $300^\circ\text{C}/\text{h}$.

3.4 Infrared Spectro Photometry

Grind the specimens of different temperatures that were subject to dry gel heat treatment into powder. Use the KBr pellet method to determine the IR absorption spectroscopy. Instrument: Type 580E (American made), wavelength range: $200\sim 4000\text{cm}^{-1}$.

3.5 Index of Refraction

Under a microscope use the Baker line moving method to determine the small glass piece index of refraction.

RESULTS AND DISCUSSION

1) The Influence of Various Factors on Gelling Time

Since the low temperature synthesis creates more types of glass, and the solution mixture's make up is complex, the factors that affect hydrolysis polymerization are therefore more numerous. Water is one reactant, and adding water clearly has an important effect. The quantity of solvent used affects the system's degree of dilution, and whether the catalytic agent is or is not useful directly influences the degree of acidity or alkalinity of the system. All of these have a large influence on the reaction outcome.

1.1 The Influence of Adding Water and the Method of Raising the Amount of Water Added-- the Two-Step Adding Water Method

In Fig.3 the data obtained from the one-step adding water method is used, where $\gamma \left(= \frac{V_{H_2O}}{V_{H_2O, (S)}} \right)$ approaches 0.5 time, liquid mixture gelling is already very speedy. After adding the $Zr(NO_3)_4$ ethanol solution, there wasn't even time to pour the mixture from the reactor before it agglomerated. If the making of glass pieces is desired, a way to increase the amount of water added should be devised so that the gel can assume a network space structure, but as stated above, once water is added large limitations are incurred. Afterwards we use the two-step adding water method. First, by adding the water this causes the $Si(OC_2H_5)_4$ to have partial hydrolysis. After the three types of materials have already been added and have been mixed together cool the mixture to room temperature, and while stirring pour in drop by drop a measured quantity of water. This way, γ can be raised to 2~3. The glass in Fig.1 was obtained using the two-step adding water method.

The hydrolysis speed of the three types of starting materials used in this work differ quite alot. If enough water and three types of starting materials are added the result will be the precipitate separating out due to speedy hydrolysis, and the synthesis reaction will have no way to be carried out. By adding the starting materials in correct order, and adding the water in different steps, the synthesis reaction is guaranteed to occur smoothly.

1.2 Amount of Solvent to Use

From Fig.4 it can be seen that, where other conditions are kept the same, an increase in the amount of solvent used causes the gelling time to be lengthened. This is because the time in which excessive amounts of solvent need to evaporate is longer. In general, a too small of amount of solvent is detrimental to the hydrolysis polyreaction. On the other hand, the gelling time is bound to greatly increase. Generally a gelling time from 2~3d is appropriate, consequently it was chosen that in this work $R\left(\frac{V_{C_2H_5OH}}{V_{H_2O} + V_{Ti(OEt)_4}}\right)$ serve as 1.

1.3 The Types and Usages of Catalytic Agents

The effects of using hydrochloric acid (HCl) and ammonium hydroxide (NH_4OH) as catalysts are seen in figures 5 and 6. When using HCl, its density relation curve showed very little value during the gelling time, this minute concentration of HCl was approximately $1.2 \times 10^{-3}N$. For the HCl comparative situations, observe figures 3 and 4, because the concentrations of HCl are not the same, the gelling process can be speeded up or delayed. When using NH_4OH , its effect can also speed up or delay the gelling process. This kind of phenomena can easily be explained using principles of colloid chemistry.

Fig.7 shows the changes in the mixed solutions' viscosity curves during the reaction system. Curve 1 shows $1.37 \times 10^{-3} N$ NH_4OH used as a catalyst, the changes in viscosity are quicker, and the gelling time is shorter. When there is no catalyst (curve 2) the changes in viscosity are slower, and the gelling time longer.

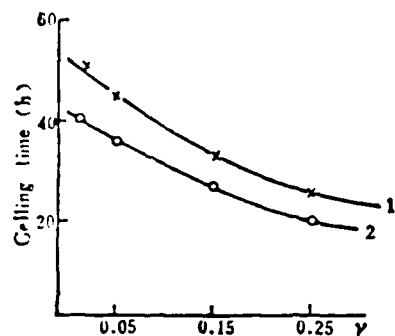


Fig.3 Gelling time vs amount of water added
1—R.H.=95%, 2—Exposure to air

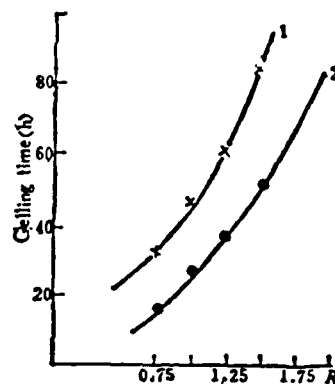


Fig.4 Gelling time vs amount of C_2H_5OH added
1—R.H.=95%, 2—Exposure to air

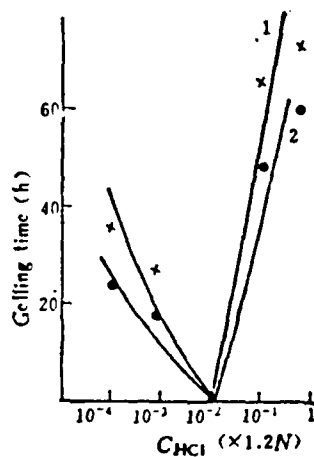


Fig.5 Gelling time vs concentration of HCl
1—R.H.=95%, 2—Exposure to air

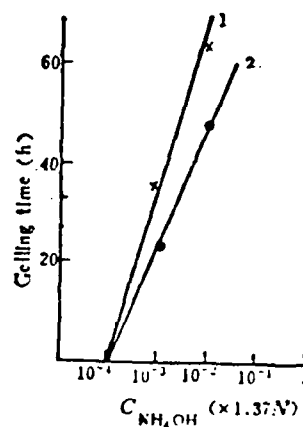


Fig.6 Gelling time vs concentration of NH_4OH
1—R.H.=95%, 2—Exposure to air

1.4 Influence of the ZrO_2 Content

Table 1 gives the ZrO_2 content, the water added to each system, the amount of solvent used and the gelling time (not having yet used a catalyst). As the ZrO_2 content increases, even though we have taken the step to increase the amount of solvent used, the amount of water which we are able to add in through the one-step adding water method, and the gelling time as well, are both greatly reduced. This is because the TiO_2 content in each system is the same. This increase in the ZrO_2 content implies a reduction in the amount of starting material $Si(OC_2F_5)_4$ used. As a result this brings about a reduction in the amount of water that can be introduced. Adding $Ti(OC_4H_9)_4$, $Zr(ON_3)_4$ hydrolysis is very easy, consequently gelling time is drastically shortened.

In another work, we studied some technological conditions in the low temperature synthesis of TiO_2-SiO_2 glass systems. For the $20TiO_2 \cdot 80SiO_2$ system, let $\gamma = 0.25$, $R=1.0$ time, and gelling time as 40h (in air). Combining the data in Table 1 it can be more clearly seen: as the system's ZrO_2 content increases, gelling time gradually reduces; when the ZrO_2 content reaches 20%, the gelling

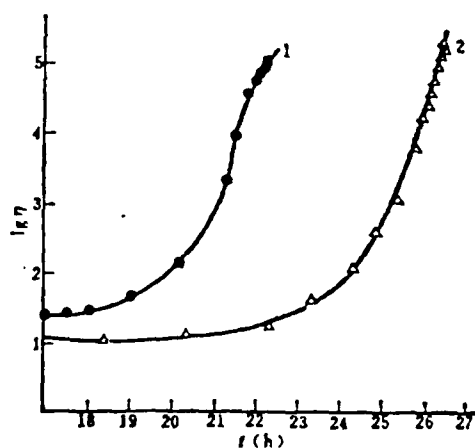


Fig.7 Change of viscosity of mixed solution 5 with time during gelling
1—With NH_4OH as catalyst, 2—Without catalyst

process is extremely speedy, the process is almost instantaneously completed.

1.5 Placement Conditions

From Figures 3 and 4 it can be discovered that in the hermetic atmosphere where relative humidity, R.H.=95%, the gelling time is longer. This is because the solvent exposed to air evaporates quickly. Longer gelling time more easily results in thorough hydrolysis polyreaction and in turn brings about a higher viscosity gel, and increases the possibility of creating glass pieces.

If the preparation conditions are not the same this will influence the gel's final state and whether or not the dry gel pieces are intact. As the dry gel pieces are exposed to air during aging time, within only five days they break into small fragments. If the mouth of the container holding the gel mass is covered up with aluminum foil, prick a small hole in the aluminum foil using a needle every day. Sixteen days later stop making the holes. Every day afterwards cover up one hole per day. By the 65th day, it will be discovered that the dry gel fragments broke into some large pieces and some small pieces; but if within two days all the holes that were punctured are covered up again, then by the 71st day the dry gel is still one whole piece. From this it is apparent that proper control of the gel mass and the surrounding interflow of air can be effective in preventing the gel piece from cracking. Moreover, the longer the aging time, the greater the shrinkage which occurs during the dry stage of the dry gel's aging time before heat treatment. As a result, during the heat treatment, the dry gels volume will contract even more, and this is beneficial towards the preparation of glass pieces.

2) The Transformation of Dry Gels into Glass During Heat Treatment

2.1 Under the two conditions of introduction of O_2 and non-introduction of O_2 , inspect the dry gels after heat treatment of them at different temperatures. Color change resulting from the added heat is seen in Table 2.

When not introducing O_2 , the blackening of the dry gels is caused by the charcoaling of organic matter. Introducing O_2 causes the organic matter to oxidize and thus be removed, solving the problem of blackening. As for the amount of oxygen to use, $1\sim 2L/min$ is adequate.

2.2 From the dry gel's DTA curve (Fig.8) the physical and chemical changes occurred when heat was added can clearly be seen. The two peak heat absorption temperatures $120^\circ C$ and $170^\circ C$ correspond to the residual moisture in the dry gels and the evaporation of the organic compounds. From $285^\circ C$ to $635^\circ C$ there is oxidation of organic material and decomposition of nitrate (NO_3^-) included inside a broad exothermic area^{110,111}. After $635^\circ C$ the curve tends to stabilize.

2.3 The infrared spectra can offer important information about the changes in composition and structure of the dry gel when heat is added. Figure 9 is the IR absorption spectra of the dry gel treated at different temperatures. The absorption peak position, corresponding vibration and the variation tendency

Table 1 Influence of the ZrO_2 content on the maximum amount of water added and the gelling time

System	γ	R	Gelling time(h) (exposure to air)
1	0.25	1.00	27
2	0.25	1.50	20
3	0.12	1.75	4
4	0.07	2.00	Instantaneously
5	0.04	2.25	Instantaneously
6	0.02	2.75	Instantaneously

with increasing temperature are all shown in Table 3.

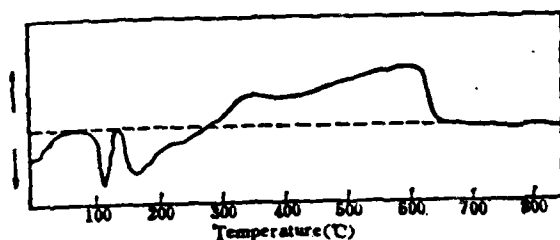


Fig.8 DTA curve of the dry gel

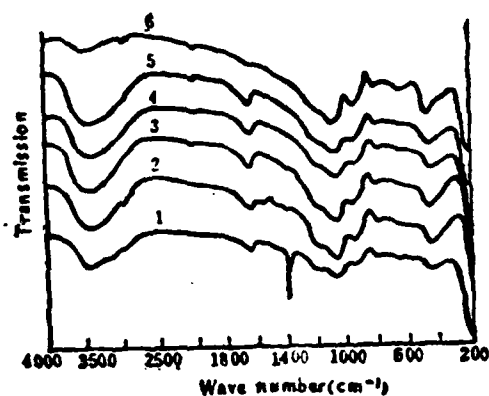


Fig.9 IR absorption spectra of the dry gel treated at different temperatures
1—100°C, 2—250°C, 3—450°C, 4—550°C,
5—600°C, 6—800°C

Table 2 Color change of the dry gel during heat treatment

Temperature (°C)	Color	
	In O ₂	In air
100	Light yellow	Light yellow
250	Light brown	Brown
450	Light yellow	Black
550	White	Black
600	White, translucent	Black
800	Colorless, transparent	Grey

Table 3 Analysis of the IR absorption spectra in fig.9

No.	Absorption peak position (cm ⁻¹)	Corresponding vibration	Variation tendency with increasing temperature	Ref.
1	3400	Si—OH, H—OH	Abating	[14]
2	1640	H—OH	Abating	[14]
3	1380	NO ₂	Abating and vanishing at 450°C	[10, 11]
4	1080	Si—O—Si	Strengthening	[8]
5	950	Si—O—Ti	Strengthening	[8]
6	800	3 + 7	No significant variation	[11]
7	450	Si—O—Si O—Si—O (flexing)	No significant variation	[11]

The absence of the peaks corresponding to the Si-O-Zr bond can be seen in Figure 9 and Table 3. This explains how Zr^{4+} is an adjusting network body that enters the glass structure, that is to say, the location of Zr^{4+} and Ti^{4+} in the glass is not the same as their function. Masayuki Nogami and Yoshiro Moriya⁽¹¹⁾ stated clearly in their study concerning the anti-alkaline stability of the amorphous $ZrO_2-TiO_2-SiO_2$ membrane and of the IR spectra that the strengthening mechanisms of Zr^{4+} and Ti^{4+} on the glass network are not the same. The Ti^{4+} attending network forms into an Si-O-Ti bond, thus Zr^{4+} then enters an empty gap in the network causing the accumulating density to increase, thereby raising the anti-alkalinity of the glass. S.P. Mukherjee and others⁽¹²⁾ have pointed out that during the low temperature synthesis of $La_2O_3-ZrO_2-SiO_2$ glass, the function of Zr^{4+} is to enter into the open gap of the silicone oxide's network structure, to strengthen the static electricity, and make the glass structure even more stable.

3) The Influence of the Heat Treatment Rising Temperature Speed on the Final Results

Under similar conditions of oxygen introduction, different rising temperature systems lead to different final results. The experiment clearly indicates: slowly rising temperature is beneficial towards the creation of glass pieces, and the key is in the rising temperature speeds during the low temperature stage ($<300^\circ C$). We carried out contrasting experiments of three different kinds of rising temperature systems: for the whole course of the heat treatment where temperatures rose at $20^\circ C/h$, in the end, glass powder was obtained; before 100° at rising temperatures of $60^\circ C/h$, $100\sim 300^\circ C$ at rising temperatures of $10^\circ C/h$, and after $300^\circ C$ at $20^\circ C/h$, what was obtained were small

pieces of glass the size of grains of rice; when during the whole course rising temperature speeds were at 10°C/h or even lower (eg. 7.5°C/h), small pieces of transparent glass were obtained as shown in figure 1. However, it should be pointed out, the speed of rising temperature is not the only important factor in deciding the final outcome. The dry gel's intrinsic quality is most important. Moreover, cracks may appear if after reaching the highest temperature the temperature is again dropped too fast.

4) Glass Refractive Indexes

Table 4 gives the theoretical calculated values and determined values of six glass compositions and their refractive indexes. Theoretical calculations are carried out using the formula $n = \sum P_i n_i^{(11)}$. P_i , n_i can be divided by each set's weight percentage content of organic matter and part refractive index. It can be observed, as the ZrO_2 content in the glass increases (coinciding with the reduction of SiO_2 content because TiO_2 content stays unchanged at 20mol%), the refractive index gradually gets larger. This explains the increase in compactness of the glass, and has a direct relationship on the increase of the capacity of the glass to be filled in or packed, caused by Zr^{4+} entering the network gaps.

Table 4 Glass compositions and their refractive indexes

System	Composition(mol%)			Refractive index	
	ZrO ₂	TiO ₂	SiO ₂	n_{calc}	n_{meas}
1	5	20	75	1.667	1.639
2	10	20	70	1.690	1.645
3	15	20	65	1.711	1.659
4	20	20	60	1.732	1.664
5	25	20	55	1.754	1.667
6	30	20	50	1.775	1.705

CONCLUSIONS

- 1) Using the gelling method in the low temperature synthesis of ZrO_2 - TiO_2 - SiO_2 glasses, small pieces of glass were produced. The study of the procedure states clearly: of one desires to reach the goal of synthesizing pieces of glass, one needs to take each starting material and add it in separately according to the hydrolysis property's weak-strong sequence, the sequential hydrolysis, and the step by step polymerization technique. Otherwise, only loose glass powder will be obtained. The step by step adding water method this procedure uses allows for the amount of water that can be added in to be greatly increased, thus guaranteeing evenly distributed transparency. It also possesses the capacity for the formation of three network-structured gel masses as well.
- 2) If one introduces into the system HCl or NH_4OH as catalysts, differing amounts of the catalyst used can have opposite effects on the gelling function. In addition their use is not easy to rigidly control, hence by the end of this work no catalyst was used at all. Through the appropriate selection of other conditions can one control the gelling time.
- 3) When performing heat treatment, the slow rising and falling of temperatures is greatly beneficial towards the creation of glass.
- 4) Zr^{4+} and Ti^{4+} each perform differently in glass, the former being a network adjusting body, the latter being a network formation body.
- 5) The sizes of the glass pieces created are still not large enough. Conditions for drying and heating stages still await further study.

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