

Synthesis of Titania-Silica Materials by Sol-Gel

*Rubia F. S. Lenza, Wander L. Vasconcelos**

*Laboratory of Ceramic Materials - LMC
Department of Metallurgical and Materials Eng. - UFMG
Rua Espírito Santo, 35 - 2^o andar, Centro, Belo Horizonte - MG, Brazil*

Received: November 21, 2000; Revised: September 23, 2002

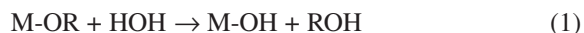
In this work TiO_2 - SiO_2 glasses containing as much as 20 mol % of TiO_2 were prepared via sol-gel process using titanium and silicon alkoxides, in the presence of chlorine, in the form of titanium tetrachloride or HCl. The gels were heat-treated until 800 °C. X-ray diffraction and Fourier transform infrared spectroscopy were used to understand the structural properties of TiO_2 - SiO_2 oxides calcined at different temperatures and to evaluate the homogeneity of these materials. The degree of the compactness of the silica network is inferred from the frequency of the asymmetric stretching vibrations of Si-O-Si bonds. Formation of Si-O-Ti bridges, as monitored by the intensity of characteristic 945 cm^{-1} – 960 cm^{-1} vibration, is particularly prominent if the method of basic two-step prehydrolysis of silicon alkoxide, addition of titanium alkoxide and completion of hydrolysis was used.

Keywords: TiO_2 - SiO_2 , sol-gel, synthesis

1. Introduction

Sol-gel is a low temperature method that produces ceramics and glasses with better purity and homogeneity than high temperature conventional process. Sol-gel has produced a wide range of compositions in several forms, such as powders, fibers, coatings, monoliths and porous membranes. The most attractive features of the sol-gel process include the production of compositions not possible with conventional ceramic preparation methods, along with the retention of the mixing level of the solution in the final product, often on the molecular scale¹⁻⁵.

The sol-gel process involves the hydrolysis (1) and condensation (2) e (3) of metal alkoxides^{4,6,7}:



By controlling the synthesis conditions carefully, these reactions may lead to a variety of structures, and to different final states for the materials^{5,6}.

The incorporation of TiO_2 into silica glasses has an important effect on the properties of the final glass. The ther-

mal stability of SiO_2 is high, but the chemical stability at high temperature in the presence of water is poor, resulting in the formation of surface hydroxyls⁷. Incorporation of TiO_2 has proven to improve the chemical stability. In addition, a small molar percentage of TiO_2 can be used to prepare silica glasses with almost zero thermal expansion coefficient due to the ability of Ti ions to coordinate tetrahedrally⁸.

Although the physical properties of the titania-silica glasses such as the thermal expansion coefficients, FTIR and Raman spectra are well documented, processing methods required to achieve and maintain an atomic distribution of titanium have been little investigated until recently. Conventional melt technology is limited for these glass compositions by the high separation of titania-rich phase at elevated temperature^{9,10}.

Recently, sol-gel process has been investigated for synthesis of TiO_2 – SiO_2 glasses^{5,7-12}. There still are problems, however, when the sol-gel processes are applied to binary systems^{11,13,14}. The reactivities of titanium alkoxides are considerably higher than for silicon alkoxides. Therefore, care has to be taken in the synthesis of binary materials of this system to avoid homo-condensation⁷. The degree of homogeneity is dependent of processing parameters, such as the nature and chemical reactivities of reactants, the concentration of water and sequence of addition, the pH of reaction

*e-mail: wlv@demet.ufmg.br

Trabalho apresentado no 14^o CBECIMAT, Águas de São Pedro, Dezembro de 2000.

medium and the time and temperature of reactions¹³.

Heterogeneity due to different hydrolysis rates can be avoided in several ways. A commonly used strategy is the use of prehydrolysis process: the slowest reacting alkoxide is prehydrolysed prior to the addition of the second, fast reacting, alkoxide. The idea is that the newly added alkoxide will condense with partially hydrolysed sites on the polymeric species formed by the preceding hydrolysis steps^{5,7,13}. Another approach consists on the control of hydrolysis rates of highly reactive alkoxide by using modified alkoxides, in which the added ligand is kinetically and/or thermodynamically more stable^{11,13}. Another mean of controlling homogeneity is achieving a very low hydrolysis rate by restricting the availability of water or prehydrolysis of the slower-reacting component with a later addition of the faster hydrolysing component, and further addition of water to complete the hydrolysis. It is expected⁵ that this method should be more suitable for producing solids that are mixed on a molecular scale.

In the present study, we focus on the influence of some preparation variables on the resulting structure of TiO₂ - SiO₂ mixed oxides that can be used as ceramic membranes⁷ and as support in catalytic systems⁵. In the mixed oxides, the weight fraction of TiO₂ was held constant at 20 mol%. The preparation variables being tested include, hydrolysis pH, the sequence of hydrolysis and mixing, the drying temperature and the influence of polymerisation control reagent.

2. Experimental

Tetraethyl orthosilicate (TEOS, Aldrich Co.) and titanium isopropoxide (TIP, Aldrich Co.) were used as precursors. Alcohol was used as solvent: ethanol (Merck Co.) and isopropanol (Química Moderna Co.). Hydrochloric acid (Merck Co.) and acetic acid (Merck Co.) were used as catalysts. As polymerisation control reagent we used TiCl₄ (Merck Co.). Binary sols are abbreviated as STX, where X is the method used in synthesis:

- (A) Two-step acid hydrolysis, where TEOS was hydrolysed with the addition of deionised water, ethanol and hydrochloric acid. The water/alkoxide molar ratio used was R = 2. After stirring for 15 minutes, a mixture of TIP, isopropanol and acetic acid was added. The pH of the solution was adjusted with hydrochloric acid to pH of 1. A second addition of water (enough to reach water/alkoxide molar ratio R = 4) was dropwised. A clear yellow solution was cast into cylindrical containers and gelled at 40 °C.
- (B) Two-step basic hydrolysis, where the acid catalyst HCl, used in the method A, was replaced by a solution of NaOH. The solution was adjusted for pH of 9.0 and precipitation occurred spontaneously to pro-

duce a powder dispersion resembling milk. Following precipitation, colloid compacts were produced by evaporation of the solvent under constant agitation. The dispersion was cast into cylindrical containers and gelled at 40 °C.

- (C) Separate prehydrolysis followed by mixing of sols. TEOS was prehydrolysed in alcoholic solution of pH 1.0 and R = 4. TIP was prehydrolysed in alcohol medium (isopropanol) with pH of 3.0 (acetic acid) and R = 4. The sols mixed under vigorous stirring for 30 min. The clear yellow solution was cast and gelled at 40 °C.
- (D) Hydrolysis of TEOS and TIP with TiCl₄ as polymerisation control reagent. The hydrolysis of binary metal alkoxides was carried out by addition, under vigorous stirring, of the mixture of TEOS and TIP in a mixture of alcohol (ethanol) and water in which the alkoxide mixture contained titanium tetrachloride as chlorine source (Cl/Ti molar ratio of 1.2). The final pH was adjusted for 0.5 with addition of HCl. The water/alkoxide molar ratio used was R = 4. The yellow solution was cast and gelled at 40 °C.

The gels were aged at 60 °C and dried at 110 °C. After drying, the gels were grounded to white fine powders and heated at 600 °C and 800 °C, maintaining the samples 6 h at each temperature.

The crystallisation behaviour of the samples was examined by X-ray diffractometry (XRD Philips Co.) using Cu Ka radiation. Diffuse reflectance FTIR (DRFTIR) spectra were recorded in a FTIR Paragon-1000 of Perkin Elmer Co. using diffuse reflectance accessory of Perkin-Elmer Co. Spectra were collected with a 4 cm⁻¹ resolution and 200 scans have been accumulated for each spectrum in the frequency range of 4400 cm⁻¹ to 400 cm⁻¹. Samples were grounded and diluted to 5% w/w with KBr salt (Merck, Co.) and were allowed to cool to room temperature in air before recording spectra. In order to compare peaks intensities, we used the same mass of each sample to obtain DRFTIR spectra.

3. Results and Discussion

STA

The DRFTIR spectra of STA samples at 110 °C, 600 °C and 800 °C are presented in Fig. 1. The spectrum at 110 °C is characterised by a dominant band at 1030 cm⁻¹ with a shoulder at 1160 cm⁻¹, assigned to asymmetric stretching vibrations, ASTO₁ and ASLO₁ modes respectively, of the tetrahedral SiO₄ co-ordination unit. The corresponding symmetric motion (STO₁) is detected at 797 cm⁻¹^{5,9}. We observed a band around 980 cm⁻¹ which is assigned as stretching vibration of silanol groups, Si-OH, owing to non-bridg-

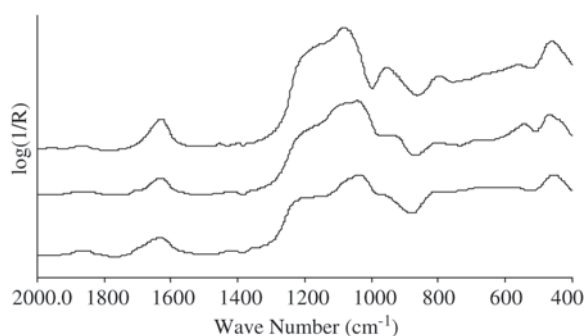


Figure 1. DRFTIR spectra of STA samples treated at 110 °C, 600 °C and 800 °C (top to bottom).

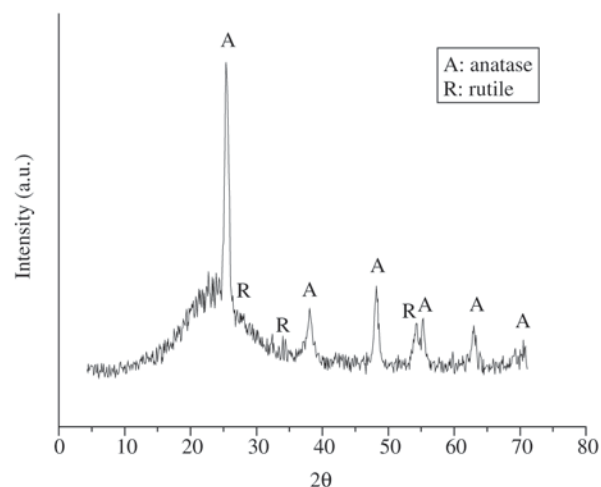


Figure 2. X ray diffraction peaks to STA sample.

ing oxygen associated to proton^{5,9,14} and a minor feature around 950 cm^{-1} , which can be associated with vibrations of Si-O-Ti bridges^{5,11}. The peak occurring at 465 cm^{-1} results from rocking vibration of Si-O-Si bonds¹⁵. The spectral features of TiO_2 can be discerned at around 540 cm^{-1} and 440 cm^{-1} . Drying this sample at 600 °C and 800 °C shifts the ASTO_1 frequency to 1032 cm^{-1} and 1074 cm^{-1} (with a shoulder at 1030 cm^{-1}), respectively. The corresponding ASLO_1 vibration mode frequencies are 1170 cm^{-1} and 1190 cm^{-1} , respectively. Calcination at high temperatures results in a considerable decrease of the 980 cm^{-1} band intensity, as compared with the corresponding gel dried at 110 °C. The weak band centred around 950 cm^{-1} , which shifted to a high frequency of 952 cm^{-1} at 800 °C, did not change its intensity. The characteristic peaks of titania (540 cm^{-1} and 440 cm^{-1}) decreased in intensity. The X-ray diffraction spectra show the presence of crystallites of anatase and rutile, as shown in Fig. 2. These results indicate that the acid two-step prehydrolysis process promotes the occurrence of low proportion of homo-condensation reactions. The STA samples calcinated at different temperatures present titania separated domains.

STB

DRFTIR spectra of mixed oxide samples prepared by a basic prehydrolysis of TEOS, addition of TIP, completion of hydrolysis, and calcination at 110 °C, 600 °C and 800 °C are presented in Fig. 3. The spectrum of gel treated at 110 °C exhibit one prominent difference from the others. A broad band between 1500 cm^{-1} and 1400 cm^{-1} , which is characteristic of organic groups¹⁵, is present. This is probably a consequence of basic hydrolysis of TEOS, which leads to an incomplete hydrolysis of alkoxide¹⁶. This band disappears at high temperatures. The ASTO_1 frequencies for gels dried at different temperatures are higher than for samples STA. At 110 °C ASTO_1 band is centred around 1075 cm^{-1} with a

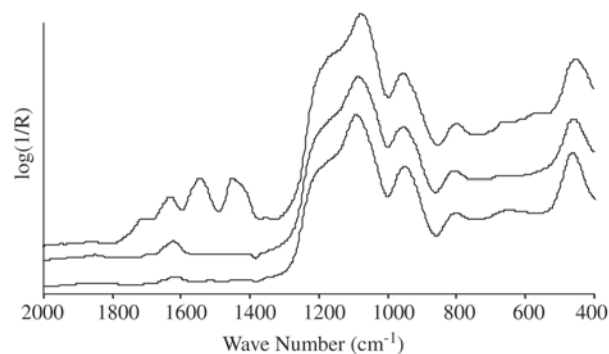


Figure 3. DRFTIR spectra of STB samples treated at 110 °C, 600 °C and 800 °C (top to bottom).

shoulder at 1170 cm^{-1} (ASLO_1). At 600 °C the frequency of this band shifts to 1080 cm^{-1} , with a shoulder at 1170 cm^{-1} and at 800 °C the frequency shifts to 1191 cm^{-1} with a shoulder at 1180 cm^{-1} . The STO_1 vibration band appears at 796 cm^{-1} at 110 °C and shifts to a high frequencies of 800 cm^{-1} with calcination. The band characteristic of Si-O-Ti bonds at around 950 cm^{-1} -955 cm^{-1} appears highly more intense than in sample STA and its intensity increase with temperature, indicating that the samples prepared by method B present more Si-O-Ti bonds. The rocking vibration band of silica network did not present any change with temperature. Interestingly, in the spectra of STB samples no spectral features of titania can be discerned. This is an indication that the samples prepared by method B did not present TiO_2 domains. No diffraction lines were observed in the X-ray spectra, only a broad peak characteristic of an amor-

phous silicate can be discerned, as can be seen in Fig. 4. These results indicate that the method B allows the preparation of homogeneous $\text{SiO}_2\text{-TiO}_2$ glasses.

STC

Diffuse reflectance FTIR spectra of mixed oxides prepared by complete hydrolysis of the components before mixing are presented in Fig. 5. The spectra of STC sample dried at different temperatures are characterised by ASTO_1 frequencies at 1070 cm^{-1} ($110\text{ }^\circ\text{C}$), 1082 cm^{-1} ($600\text{ }^\circ\text{C}$), and 1086 cm^{-1} ($800\text{ }^\circ\text{C}$). The ASLO_1 frequencies also shift to higher frequencies with the increasing of temperature. The STO_1 band vibration appears at 794 cm^{-1} at $110\text{ }^\circ\text{C}$ and its frequency shifts to a high frequency of 800 cm^{-1} with calcination. The intensity of SiOH absorption band decreases with the increasing of temperature. The Si-O-Ti band appears at 950 cm^{-1} (weak) and its intensity also decreases

upon heating. The band due to titania network appears at 560 cm^{-1} . These spectra denote that samples obtained by method C present titania domains with low proportion of Si-O-Ti bonds. The X-ray diffraction spectrum, shown in Fig. 6, denotes the presence of crystallisation of titania (anatase and rutile). Thus, we conclude that the method of complete hydrolysis of the two alkoxides before mixing is not adequate for preparing homogeneous binary glasses.

STD

The DRFTIR spectra of mixed oxide SiO_2 and TiO_2 prepared using TiCl_4 as polymerisation control reagent are shown in Fig. 7. The ASTO_1 frequency of the sample treated at $110\text{ }^\circ\text{C}$ appears at 1075 cm^{-1} and shifts to 1086 cm^{-1} at $800\text{ }^\circ\text{C}$. The ASLO_1 and STO_1 band frequencies also shift to higher frequencies with the increasing of temperature. The intensity of silanol band decreases with calcination. The

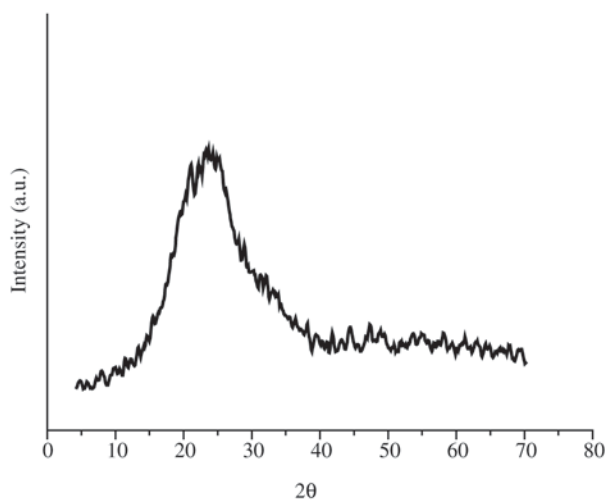


Figure 4. X ray diffraction peaks to STB sample.

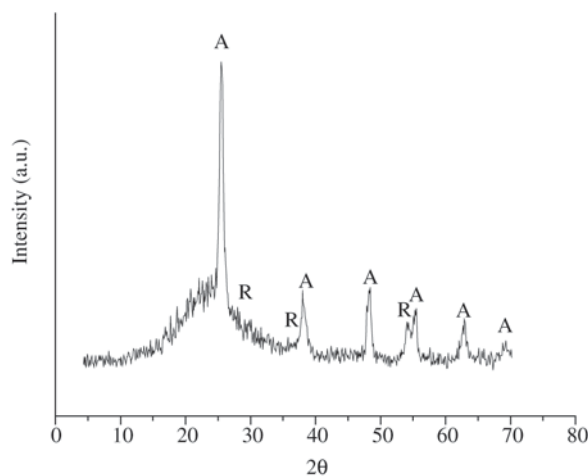


Figure 6. X ray diffraction peaks to STC sample.

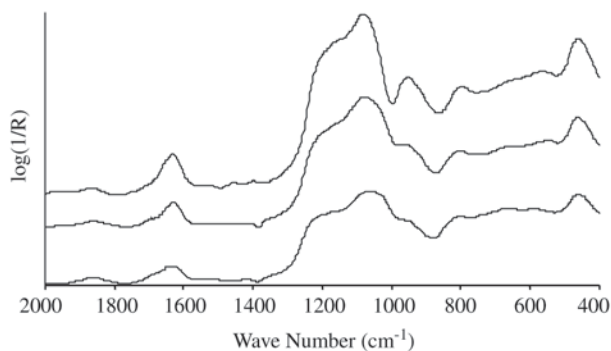


Figure 5. DRFTIR spectra of STC samples treated at $110\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ (top to bottom).

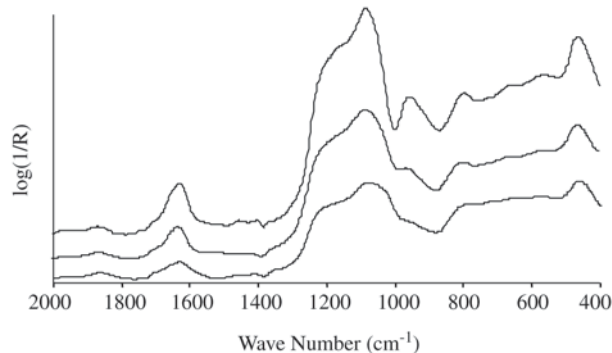


Figure 7. DRFTIR spectra of STD samples treated at $110\text{ }^\circ\text{C}$, $600\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ (top to bottom).

characteristic band of Si-O-Ti bridges appears around 950 cm^{-1} and its intensity stays roughly constant with the increasing of temperature. The titania characteristic bands (560 cm^{-1} and 440 cm^{-1}) are present for all temperatures studied. The X-ray diffraction spectrum of the STD sample is presented in Fig. 8. This spectrum shows the titania crystallisation in anatase phase. We noted that samples obtained by method D and dried at $800\text{ }^\circ\text{C}$ present a heterogeneous network with separated oxides and a low amount of Si-O-Ti bridges.

We would expect that TiCl_4 could avoid the homo-condensation reactions by the exchange reaction with titanium isopropoxide¹¹:



Although the replacement of alkoxy groups by chlorine decreases the degree of association of titanium alkoxide, which could prevent preferential segregation of titanium and silicon oxides, the result indicates the occurrence of homo-condensation reactions. Thus, we can conclude that a large amount of chlorine is required to avoid homo-condensation reactions.

The positions of the maxima ASTO_1 vibration mode of Si-O-Si bonds, which may serve as indication of the degree of cross-linking of the silica network, are highest in the spectra of the gels prepared by the two-step basic prehydrolysis of silicon alkoxide method. This is expected since the basic medium promotes high rates of polymerisation and consequently, a more compact oxide network.

An ideal TiO_2 - SiO_2 gel would consist only of Si-O-Si and Si-O-Ti bonds, which can be detected by means of FTIR. If the gel were not homogeneous, crystallisation of TiO_2 would occur and be detected by XRD. The band in the

$945\text{ cm}^{-1} - 960\text{ cm}^{-1}$ range is typical for TiO_2 - SiO_2 glasses or crystalline titanium-silicate^{5,9}. It has been assigned to a local impurity mode of a SiO_4 structural unit bonded to Ti^{IV} (*i.e.*, the stretching modes of Si-O-Ti bridges). The relative intensity of this characteristic absorption can be used to evaluate the amount of Ti^{IV} cations incorporated into the silica network in tetrahedral co-ordination^{5,9}. It can be noted that only STB samples present this band with high intensity, indicating that method B promotes the formation of a high proportion of hetero-condensation reactions. In addition, the lack of features due to titania in the spectra of STB samples indicates absence of TiO_2 domains. The X-ray diffraction spectra confirm these observations: only in the spectra of STB samples no diffraction lines were observed.

4. Conclusion

Sol-gel derived glasses in the TiO_2 - SiO_2 system, obtained through methods A, C and D, are heterogeneous in terms of TiO_2 distribution. As far as cross-linking of the silica network is concerned, hydrolysis in basic and/or high temperature drying promote the formation of strongly cross-linked networks.

An intense signal due to Si-O-Ti bridges, the lack of features of TiO_2 domains on the DRFTIR spectra and X-ray diffraction spectra attest that method B is adequate to preparing homogeneous TiO_2 - SiO_2 glasses with a high content of TiO_2 and a highly compact oxide network.

Acknowledgement

The authors thank the financial support of CAPES, CNPQ and FAPEMIG.

References

1. Alkoxysilane – [Http://www.b72.com/objects/stone_axhome.html](http://www.b72.com/objects/stone_axhome.html) – 16/10/98.
2. Sham, E.L.; FÁrfan-Torres, E.M.; Michel, R.L.; Gottifredi, J.C. *Latin America Applied Research*, v. 27, p. 245, 1997.
3. Hu, L.; Yoko, T.; Kozuka, H.; Sakka, S. *Thin Solid Films*, v. 219, p. 18, 1992.
4. Lenza, R.F.S.; Vasconcelos, W.L. *Journal of Non-Crystalline Solids*, v. 263, n. 1-3, p.164, 2000.
5. Schraml-Marth, M.; Walther, K.L.; Wokan, A.; Handy, B.E.; Baiker, A. *Journal of Non-Crystalline Solids*, v. 143, p. 93, 1992.
6. Brunet, F.; Cabane, B. *Journal of Non-Crystalline Solids*, v. 163, p. 211, 1993.
7. deLange, R.S.A.; Hehink, J.H.A.; Kelzer, K.; Burggraaf, A.J. *Journal of Non-Crystalline Solids*, v. 191, p. 1, 1995.
8. Salvado, J.M.M.; Margaça, F.M.A.; Teixeira, J. *Journal of Non-Crystalline Solids*, v. 163, p. 115, 1993.
9. Minehan, W.T.; Messing, G.L.; Pantano, C.G. *Journal of*

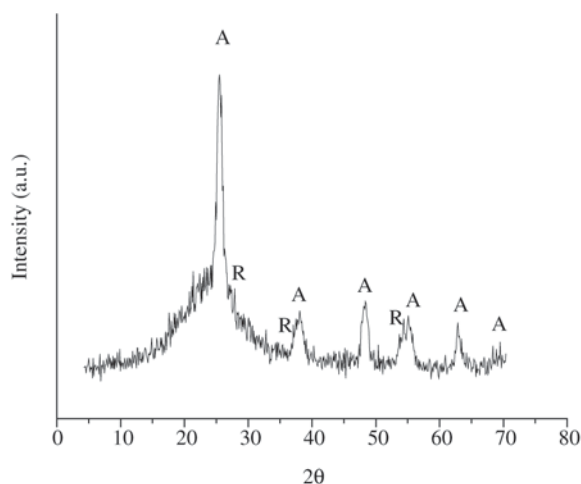


Figure 8. X-ray diffraction peaks to STD sample.

- Non-Crystalline Solids*, v. 108, p. 163, 1989.
10. Deng, Z.; Breval, E.; Pantano, C.G. *Journal of Non-Crystalline Solids*, v. 100, p. 365, 1988.
 11. Aizawa, M.; Nosaka, Y.; Fujii, N. *Journal of Non-Crystalline Solids*, v. 168, p. 49, 1994.
 12. Martucci, A.; Schell, J.; Battaglin, G.; Guglielmi, M. *Journal of Applied Research*, v. 27, p. 245, 1997.
 13. Pereira, M.M.; Clarck, A.E.; Hench, L.L. *Journal of Materials Synthesis and Processing*, v. 2, n. 3, 1994.
 14. Orgaz, F.; Rawson, H. *Journal of Non-Crystalline Solids*, v.82, p.378, 1986.
 15. Lenza, R.F.S.; Vasconcelos, W.L. *Materials Research*, v. 4, p. 189, 2001.
 16. Brinker, C.J.; Scherer, G.W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press, inc. San Diego, CA. P. 907, 1990.