

Sol-gel processing of tellurite powder

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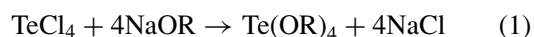
Tellurium ethoxide is highly sensitive to moisture in air and water. The hydrolysis and condensation of tellurium ethoxide exposed under different levels of water and moisture are investigated in this work and the hydrolysis products were characterised by infrared spectrometry and X-ray diffraction. The decomposition process of the product of tellurium ethoxide hydrolysed in air was analysed by differential scanning calorimetry and thermogravimetry. This work also studied the influence of sodium component on the phase transformation of the hydrolysis product in the decomposition process and on the morphology of the heat-treated hydrolysis products.

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1. Introduction

Tellurite (TeO_2) materials have been studied for some years due to their high refractive index [1], good non-linear optical properties [2] and electrical semiconductivity [3]. The unusual nature and potential applications of tellurite materials are largely attributed to their structures. In tellurite glasses and crystalline tellurite, the basic structural unit is $[\text{TeO}_4]$ with a trigonal bipyramid structure, in which there are two equatorial Te-O bonds, two axial Te-O bonds and one lone pair of electrons of tellurium atom occupying the third equatorial position.

Sol-gel processing is an attractive method to prepare ceramic materials since the variety of preparative methods and ready availability of a large number of starting materials have provided the feasibility to produce various materials [4]. Tellurium alkoxides ($\text{Te}(\text{OR})_4$), as precursors for sol-gel processing of tellurite materials, were successfully synthesised by reacting tellurium tetrachloride with sodium alkoxides (reaction (1)) [5], but up to date the study of sol-gel processing of tellurite



powders has been limited to the work carried out by Pierre *et al.* in 1994 [6]. Their work showed that the tellurium alkoxide was hydrolysed to form tellurite powders, however, it failed to separate the tellurium alkoxide from NaCl, the by-product of reaction (1) in the synthesis process, consequently the existence of a large amount of NaCl in the tellurium alkoxide and in its hydrolysis products casts some doubts on the explanations on the phase transformation of the hydrolysis products by the authors since sodium ion is a well-known glass modifier and can change the phases transformation process of tellurite materials [7]. The present study focuses on investigating the hydrolysis and condensation of tellurium ethoxide ($\text{Te}(\text{OEt})_4$), the decomposition process of its hydrolysis products and the influence of

the sodium component on the phase transformation of the hydrolysis product.

2. Experimental

The hydrolysis behaviour of tellurium ethoxide under different levels of water exposure was investigated. A 0.1M solution of $\text{Te}(\text{OEt})_4$ (InorgTech, 99.9%) in anhydrous ethanol was prepared under argon in a glove box. 10 ml of this solution was exposed for 1 day to an environment with 1.0% humidity in glove box and to ambient conditions respectively. Alternatively the solution was added with different amounts of water at $\text{H}_2\text{O} : \text{Te}(\text{OEt})_4$ molar ratios (r_h) of 1 : 1 and 100 : 1 respectively. The hydrolysis products were kept at room temperature for 1 day before being dried under vacuum. To study the influence of sodium component on the phase transformation of the hydrolysis product, sodium ethoxide, made by reacting metallic sodium with anhydrous ethanol in a dry environment, was added to $\text{Te}(\text{OEt})_4$ solutions to give 6.3 mol% and 12.7 mol% sodium components respectively. The mixing solutions were exposed on ambient conditions for one day in order to be hydrolysed and dried.

The hydrolysis products were characterised by infrared spectrometry (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Thermal analysis was carried out by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) over a temperature range of 60–580°C in air with a heating rate of 10°C/min in order to study the decomposition process of the hydrolysis product.

3. Results and discussion

3.1. Hydrolysis and condensation of $\text{Te}(\text{OEt})_4$

When 0.1 M $\text{Te}(\text{OEt})_4$ solution was exposed in an environment with 1.0% humidity, a light yellow powder formed after the evaporation of solvent. The solution

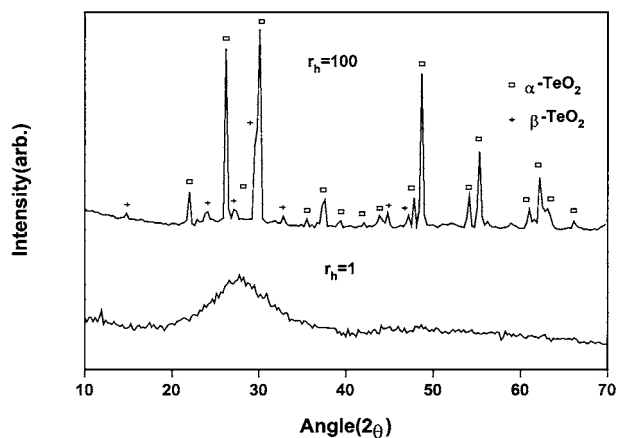
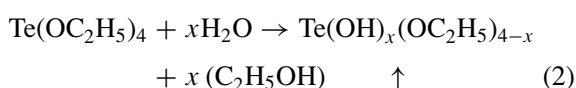


Figure 1 XRD results of the products of $\text{Te}(\text{OEt})_4$ hydrolysed in the solutions with $\text{H}_2\text{O} : \text{Te}(\text{OEt})_4$ molar ratios of 1 : 1 ($r_h = 1$) and 100 : 1 ($r_h = 100$) respectively. The products hydrolysed in a 1.0% humidity environment and in air gave similar XRD results to that of the product from $r_h = 1 : 1$.

exposed in air for 1-2 minutes formed a white precipitate during this period, which gave a voluminous white powder. Adding a small amount of water ($r_h = 1 : 1$) to 0.1M $\text{Te}(\text{OEt})_4$ solution resulted in the immediate production of a white precipitate, which formed a white powder after being dried. XRD patterns of these three products, as represented in Fig. 1, exhibited no sharp diffraction peaks, indicating an amorphous nature. When more water ($r_h = 100 : 1$) was added to the $\text{Te}(\text{OEt})_4$ solution, a fine white precipitate formed, which subsequently transformed to a yellow powder after ageing in the parent solution for one day. XRD results (Fig. 1) showed the formation of $\alpha\text{-TeO}_2$ with a small amount of $\beta\text{-TeO}_2$.

The FTIR spectrum of the product obtained from $\text{Te}(\text{OEt})_4$ hydrolysed in 1.0% humidity, as shown in Fig. 2, exhibits a broad absorption band at 635 cm^{-1} and a shoulder around 760 cm^{-1} , which may be attributed to Te-O bonds in accordance with those of tellurite glasses [8, 9]. The broadening of the band at 635 cm^{-1} is attributed to a distribution of $[\text{TeO}_4]$ units that have slightly various lengths of Te-O bonds in the hydrolysis product, as observed in a previous study on tellurite glasses [10]. The absorption bands due to the ethyl groups in $\text{Te}(\text{OEt})_4$, such as 1480, 1380, 1090, 1050, 880 cm^{-1} , are largely reduced in intensity, but the bands around 3320 cm^{-1} and 1630 cm^{-1} due to OH groups occur. These results suggest that the following reaction (2) happened:



The FTIR spectrum (Fig. 2) of the product hydrolysed in air shows that the absorption bands due to the ethyl groups are further weakened or disappear, whilst the intensities of absorption bands corresponding to the hydroxyl groups at 3320 and 1630 cm^{-1} are increased, indicating that the hydrolysis reaction (reaction (2)) was enhanced with the increase of moisture. With the increase of water content to $r_h = 1 : 1$, the shoulder around

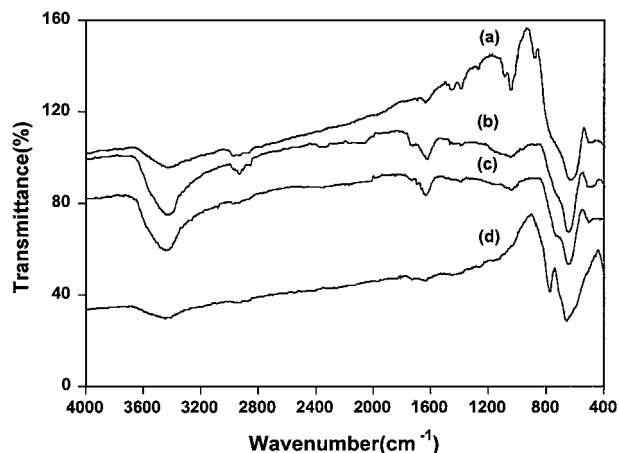
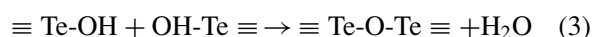


Figure 2 FTIR spectra of the products hydrolysed in different conditions (a) in glove box (b) in air (c) in water with $r_h = 1$ (d) in water with $r_h = 100$.

770 cm^{-1} due to Te-O bonds becomes more apparent and almost no absorption bands of the ethyl groups exist, suggesting the completion of the hydrolysis reaction. With the further increase of water ($r_h = 100 : 1$), three absorption bands occur at 635 , 670 and 770 cm^{-1} , which are typical in crystalline tellurite [9], whilst the bands due to OH groups are weakened. These results, together with XRD results (Fig. 1), indicate that the condensation reaction between the hydrolysed species happened with a oxolation mechanism shown as reaction (3), and resulted in the crystalline tellurite. The formation of crystalline TeO_2 products was also found by Pierre *et al.* in their study [6].



3.2. Decomposition process of the product hydrolysed at ambient conditions

The results of DSC and TG analysis on the product of $\text{Te}(\text{OEt})_4$ hydrolysed in air are shown in Fig. 3 and XRD results of the hydrolysis products heat treated at various temperatures are given in Fig. 4.

At heat treatment temperatures below 200°C , DSC and TG results show an endothermic process with about

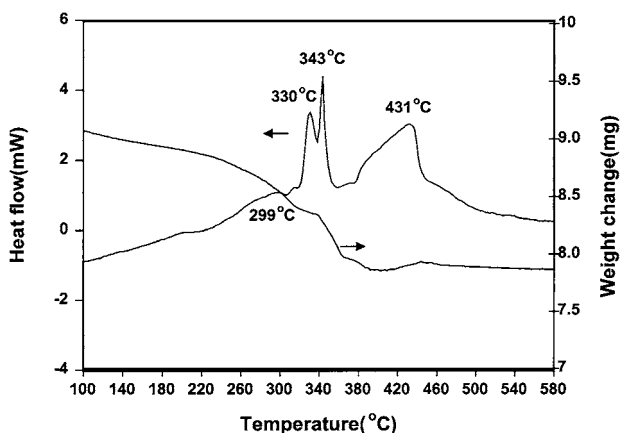


Figure 3 DSC and TG results of the product of $\text{Te}(\text{OEt})_4$ hydrolysed in air with a heating rate of $10^\circ\text{C}/\text{min}$.

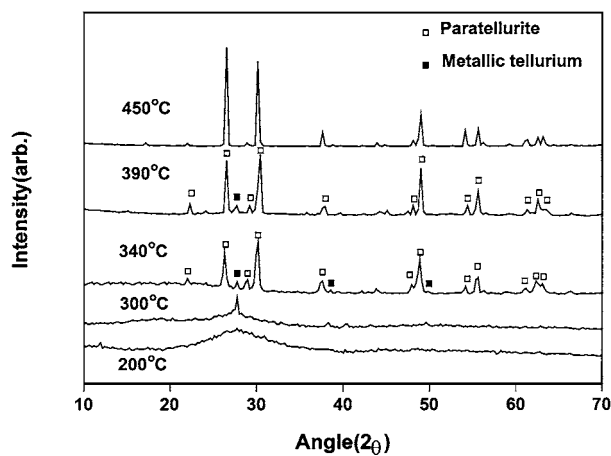


Figure 4 XRD results of the product of $\text{Te}(\text{OEt})_4$ hydrolysed in air after heat-treatment at different temperatures.

3% weight loss, which is attributed to the evaporation of organic components and desorption of water. XRD results (Fig. 4) show that the product heat treated in this temperature range was amorphous. At temperatures in the range of 200–300°C, there is a broad exothermic peak with corresponding weight loss of 4.3% and XRD results exhibit the presence of metallic tellurium, indicating that organic groups in the hydrolysis product started to decompose with the occurrence of the reduction reaction to give metallic tellurium. At temperatures between 320–340°C, an exothermic peak occurs with little weight loss ($\approx 1\%$). XRD results show the formation of crystalline $\alpha\text{-TeO}_2$, therefore, the exotherm can be attributed to the crystallisation of tellurite. At slightly higher temperature (340–360°C), another exothermic peak appears with around 4.5% weight loss, suggesting the combustion of organic components. At temperatures between 380–460°C, an exothermic peak appears with slight increase of weight. XRD results on samples heat treated at 450°C show the disappearance of metallic tellurium, indicating that the exotherm and the weight gain was due to the oxidation of metallic tellurium that was formed at lower temperatures.

3.3. Influence of sodium component on the phase transformation in decomposition process

The thermal analysis results of the hydrolysis products with different sodium contents are shown in Fig. 5. The influence of sodium component on the temperature of forming crystalline tellurite was investigated by XRD (Fig. 6).

In zone 1 of Fig. 5, the decomposition process was mainly the evaporation or break-down of organic groups, followed by their combustion with the formation of tellurium and deposition of carbon [11, 12]. The hydrolysis products containing sodium component exhibit more distinct exothermic peaks and higher decomposition temperatures. This may be due to the introduction of more organic groups in the hydrolysis products by sodium ethoxide since it is more stable in air than $\text{Te}(\text{OEt})_4$, consequently more organic component remaining in the products without being completely hy-

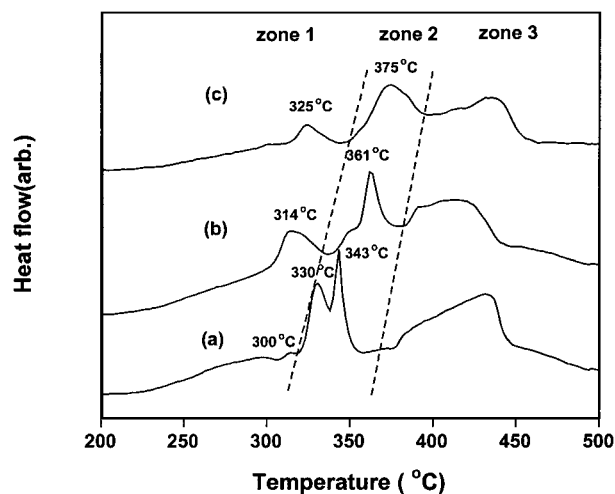


Figure 5 DSC results of the products of $\text{Te}(\text{OEt})_4$ hydrolysed in air with different sodium contents (a) sodium content: 0 (b) sodium content: 6.3 mol% (c) sodium content: 12.7 mol%.

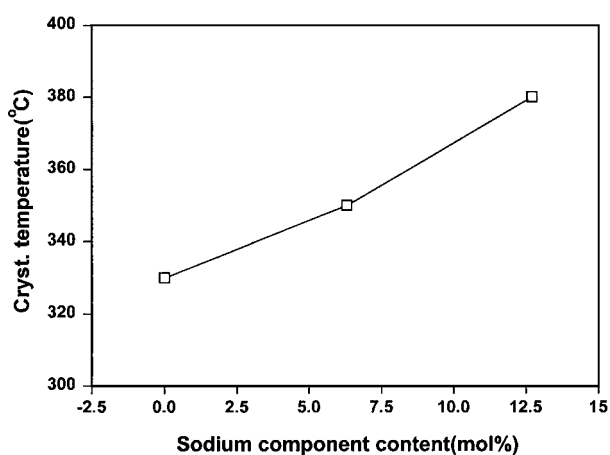


Figure 6 Relationship of tellurite crystallisation temperature with sodium content, measured by XRD.

drolysed. In zone 2, the two exothermic peaks in the sodium-free sample, which were related to crystallisation and combustion of carbon respectively, gradually overlap each other in the sodium-contained samples. The reason is that the increase of the sodium content causes an increased crystallisation temperature, as shown in Fig. 6, therefore, the peak due to the crystallisation moves to higher temperatures and overlap with another one. In zone 3, the exothermic peaks observed by DSC can be attributed to the oxidation of tellurium, as explained on Fig. 3, and the sodium content did not influence this process significantly.

Sodium oxide is well known as a modifier in glasses, which can provide the non-bridging oxygen atoms to glass formers. The ionic field strength Z/r^2 (Z : the charge of cations, r : the ionic radius of cations) was applied to describe the ability of cations to attract the oxygen ion in glasses [13]. The higher the ionic field strength of an atom, the more strongly does it attract the oxygen atom. In sodium-contained tellurite materials, the ionic field strength of the tellurium atom and the sodium atom are 4.4 and 2.3 respectively, suggesting that tellurium ions are more capable to attract oxygen ions than sodium ions. Consequently, the tendency of

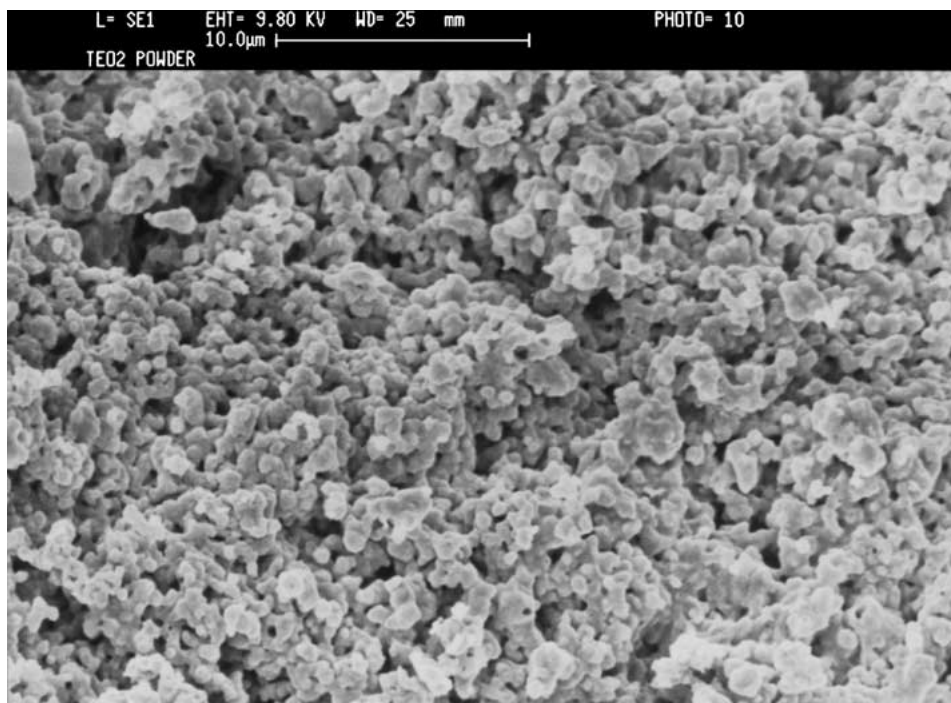


Figure 7 Morphology of the $\text{Te}(\text{OEt})_4$ hydrolysis sample heat treated at 650°C in an alumina crucible in static air for 30 minutes, observed by SEM.

tellurium ions to be surrounded by the greatest number of oxygen atoms possible can be partly satisfied in the presence of Na_2O , without the need for polymerisation of the $[\text{TeO}_4]$ units by sharing corners, which resulted in a portion of the oxygen bridges between $[\text{TeO}_4]$ tetrahedra being broken and gave non-bridging oxygen atoms, as sodium oxide did in other oxide glasses [14]. Therefore, sodium oxide component hindered the crystallisation of tellurite in the decomposition process of the hydrolysis products, as indicated by XRD results in Fig. 6.

When the temperature of heat treatment was increased, the increased thermal diffusion rate of ions eventually allowed the nucleation and growth of crystal grains. Two factors may promote the crystallisation process in the sol-gel derived tellurite materials, according to Zanotto's study on other oxide materials [15]. Firstly, the residual carbon and metallic tellurium particles would be anticipated to provide numerous positions for heterogeneous nucleation. Secondly, the thermal process crossing the temperature range of nucleation and growth was rather slow (the heating rate being $10^\circ\text{C}/\text{min}$ in the thermal analysis), which also provided opportunities for crystallisation. Similar phenomena were found even in some readily glass forming systems, such as 15 mol% Li_2O –85 mol% SiO_2 glasses, in attempts to prepare glasses without melting by a sol-gel route [16].

The products from the hydrolysis of pure $\text{Te}(\text{OEt})_4$ in air gave yellow particular α - TeO_2 after heat treatment at 650°C in air for 30 minutes in alumina crucibles. No apparent contamination was observed on the interface between the powder sample and the crucible. The morphology of the sample is shown in Fig. 7. Particles are bonded together due to sintering, but no apparent glassy phase is observed. When samples containing 12.7 mol% sodium component heat-treated at 650°C , it adhered to the alumina crucible. The surface mor-

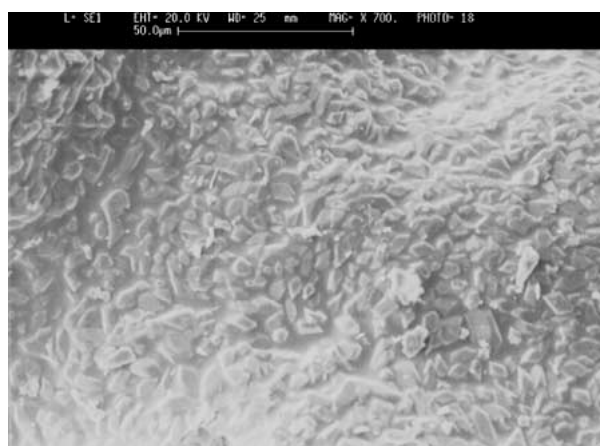


Figure 8 Morphology of the surface of the hydrolysis sample with 12.7 mol% Na, heat treated at 650°C in an alumina crucible in static air for 30 minutes, observed by SEM.

phology of the sample (Fig. 8) shows large crystalline particles bonded by a glassy phase.

The present experimental results are different from those reported by Pierre *et al.* [6] in two aspects. Firstly, the crystallisation temperature of α - TeO_2 observed in this work was about 50 – 70°C lower than that reported by them. Secondly, the product hydrolysed from pure $\text{Te}(\text{OEt})_4$ gave a particular α - TeO_2 after heat-treatment at 650°C in the alumina crucible, rather than a tellurite melt as described in Pierre *et al.*'s work, and no apparent reaction was observed between the hydrolysis product and the alumina crucible. The higher crystallisation temperature and the melting at 620°C observed by them were probably not due to the reactions between the hydrolysis product and alumina or platinum crucibles as they concluded, but rather these phenomena should be attributed to the affect of sodium component according to this study, which, as a by-product of synthesising

the tellurium alkoxide, was not separated from the tellurium alkoxide in their work.

4. Conclusions

Tellurium(IV) ethoxide was found to be very sensitive to water and atmospheric moisture. The hydrolysis and condensation reactions were enhanced with the increase of water content. The tellurium ethoxide products hydrolysed in glove box, in air and in the solution with a small amount of water were amorphous, whilst the hydrolysis in a large amount of water gave crystalline tellurite. In the decomposition process of the amorphous hydrolysis product, crystalline α -TeO₂ formed at the temperature range of 320–340°C. Metallic tellurium was found to be formed at lower temperatures, which was oxidised at higher temperatures in air to give α -TeO₂. The existence of sodium component in the hydrolysis products resulted in the increase of tellurite crystallisation temperature and the formation of glass phase during the heat treatment at higher temperatures, which can explain the discrepancies between the present work and Pierre *et al.*'s previous study.

References

1. H. YAMAMOTO, H. NASU and J. MATSUOKA, *J. Non-Cryst. Solids* **170** (1994) 87.
2. M. E. LINES, *J. Appl. Phys.* **69** (1991) 6876.

3. H. HIRASHIMA, M. IDE and T. YOSHIDA, *J. Non-Cryst. Solids* **86** (1986) 327.
4. L. G. HUBERT-PFALZGRAF, *New J. Chem.* **11** (1987) 663.
5. R. C. MEHROTRA and S. N. MATHUR, *J. Indian Chem. Soc.* **42** (1965) 1.
6. A. PIERRE, F. DUBOUDIN, B. TANGUY and J. PORTIER, *J. Non-Cryst. Solids* **147/148** (1992) 569.
7. R. A. EL-MALLAWANY, *J. Appl. Phys.* **72** (1992) 1774.
8. N. MOCHIDA, K. TAKAHASHI, K. NAKATA and S. SHIBUSAWA, *Yogyo-Kyokai-shi* **86** (1978) 317.
9. J. C. SABADEL, P. ARMAND and D. CACHAU-HERREILLAT, *J. Solid State Chemistry* **132** (1997) 411.
10. S. K. J. AL-ANI, C. A. HOHARTH and R. A. EL-MALLAWANY, *J. Mater. Sci.* **20** (1985) 661.
11. S. SAKKA and K. KAMIYA, *J. Non-Cryst. Solids* **42** (1980) 403.
12. B. E. YOLDAS, *J. Mater. Sci.* **21** (1986) 1087.
13. H. STEVENS, in "Introduction to Glass Science," edited by L. Pye, H. Stevens and W. Lacourse (Plenum Press, New York, 1972) p. 197.
14. Y. HIMEI, A. OSAKA, T. NANBA and Y. MIURA, *J. Non-Cryst. Solids* **177** (1994) 164.
15. E. D. ZANOTTO, *ibid.* **147/148** (1992) 820.
16. C. J. BRINKER and G. W. SCHERER, "Sol-Gel Science—The Physics and Chemistry of Sol-Gel Processing" (Academic Press, Inc., U.S.A., 1990).

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