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Journal of Non-Crystalline Solids 276 (2000) 56–60

JOURNAL OF  
NON-CRYSTALLINE SOLIDS

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# Decrease of interlamellar spacing of silica samples induced by external pressure

Robson F. de Farias<sup>a</sup>, Leandro Martinez<sup>b</sup>, Claudio Airoidi<sup>b,\*</sup>

<sup>a</sup> Departamento de Química, Universidade Federal de Roraima, 69310-270 Boa Vista, Roraima, Brazil

<sup>b</sup> Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970 Campinas, São Paulo, Brazil

Received 10 November 1999; received in revised form 26 April 2000

## Abstract

Lamellar silica and cadmium or mercury derivative-doped samples were synthesized by neutral amine route through the sol–gel process. These samples showed a decrease of the interlamellar *d*-space promoted only by an increase of the externally applied pressure on the samples. For a constant external pressure the observed decrease has a linear behavior as a function of time. The undoped lamellar silica, when pressed under 760 mPa for 45 min, exhibited a decrease of the interlamellar distance of 16%. The obtained results suggested that under an increased external pressure, cadmium is forced to change its coordination environment, to adjust to a most stable structure. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

A templating process that mimics biomineralization has been used to synthesize many highly organized material systems. The self-organization of molecules into a highly ordered structural architecture provides new materials with many possible applications, such as selective adsorption of toxic compounds from water and the immobilization of photo active species [1].

Low-temperature synthetic procedures, such as those used in sol–gel [2], have been successfully employed as a method to obtain silica samples of lamellar or hexagonal structures [3–5]. In such a kind of synthesis, neutral *n*-alkylamines [3], dial-

kylamines [4], alkylammonium bromide salts [6–8] or alkyltrialkoxysilanes [9] can be employed as template molecules to produce lamellar compounds. After establishing the host–guest interaction the interlayer *d*-spacing shows a linear relationship with the carbonic chain length of the template species [10].

Structural transitions related to conversion of lamellar to hexagonal stages can be promoted for such kinds of inorganic–organic matrices, which are dependent on the total amount of water [3] or pH of the reactions [11,12]. On the other hand, the same behavior can be detected through the thermal effects, by disturbing the guest molecule interaction with the inorganic backbone, causing the release of the template molecules from the original structure in the heating process [13].

The addition of transition metal salts, such as copper nitrate [14] or the solid state reaction of copper nitrate or sulphate modified samples with

\* Corresponding author. Tel.: +55 192 397 766; fax: +55 197 883 023.

E-mail address: airoidi@iqm.unicamp.br (C. Airoidi).

potassium bromide [15] can also exert a remarkable influence on the structure of lamellar silica samples. In such a procedure, a decrease of the interlayer  $d$ -space is also observed, which is dependent on the total concentration, as well as on the coordination features of the cation involved. However, the participation of the counter anion in these matrices from the point of view of coordination, is also an important feature to be considered in studying structural changes [14,15].

The aim of this publication is to report the influence of the increase of the external pressure on lamellar silica and cadmium or mercury derivative-doped samples, which effect can cause a contraction of the interlayer space, with a new adjustment of the cation coordination in the final stable structure.

## 2. Experimental

The lamellar silica was prepared as previously described [14,15]. Briefly,  $1.0 \times 10^{-2}$  mol of 1,12-diaminododecane (DADD) is added to a mixture of 0.50 mol of *n*-propanol and 3.30 mol of water. This solution was stirred for 10 min to obtain a homogeneous phase. To this mixture,  $1.0 \times 10^{-2}$  mol of tetraethylorthosilicate (TEOS) was added through a syringe and, after 3 min, the gel was formed. This resulting product was aged for 24 h at room temperature and dried under vacuum for 8 h at 80°C.

Cadmium and mercury doped samples were prepared after adding 10.0 mmol of  $\text{CdCl}_2$  or  $\text{HgCl}_2$  to the silicate gel previously aged for 48 h. The mixture was stirred for 25 min and then aged for another 24 h. The final metal-doped silicate was dried as occurred with the lamellar sample.

The X-ray diffraction patterns were obtained by using a Shimadzu diffractometer employing  $\text{CuK}\alpha$  radiation (35 kV, 25 mA). The prepared samples containing lamellar compounds were pressed on a uniaxial press under  $760 \pm 38$  mPa for times ranging from 5 to 45 min, before any measurement. For this operation 45 min was chosen as the maximum time in which any variation in the pressure could be avoided.

In all cases, a mass of 0.20 g was employed to produce the desired discs that presented a cross-sectional area of 1.30 cm<sup>2</sup>. A Perkin–Elmer device that is normally used for infrared technique was employed to obtain the discs, and the total area of the platens was directly pushed on the samples.

For each established pressure at least two samples were employed for all matrices. The X-ray patterns were recorded twice for each sample prepared. In spite of these experimental precautions,  $2\theta$  values were measured with a deviation of  $\pm 0.05$  degree, which did not imply any observable difference in the interlayer  $d$ -values.

## 3. Results

The X-ray diffraction patterns for the synthesized silica and those pressured samples under 760 mPa for 15 min are shown in Fig. 1. As can be observed, the unpressed silica sample exhibited three orders of 001 reflections, whereas, for the pressed one, four orders were detected. Furthermore, a decrease in the interlayer distance can be observed for the lamellar pressed sample. The unpressed sample exhibited diffraction peak values for  $2\theta$  at 3.8; 7.3 and 11.5 degrees, due to 001, 002 and 003 diffraction planes, which can be related to  $d$ -spacings of 2.3, 1.2 and 0.8 nm, respectively. For the pressed sample the peaks corresponding to  $d$ -spacings of 001, 002, 003 and 004 gave the values 2.0, 1.0, 0.7 and 0.5 nm,

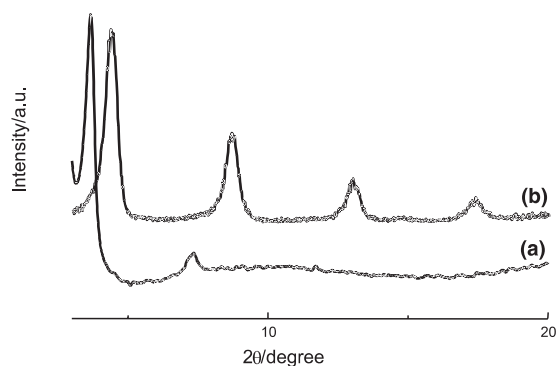


Fig. 1. X-ray diffraction pattern for synthesized lamellar silica (a) and lamellar silica pressed under 760 mPa for 15 min (b).

respectively. The interlamellar distance for 001 diffraction plane for the pressed lamellar silica samples, exhibited a linear relationship, when  $d$ -values are plotted as a function of time, as shown in Fig. 2, to give an excellent coefficient of correlation equal to 0.9999. However, a decrease of the interlayer distance (nm) with time (min), under constant pressure can be observed. From the resulting plot, Eq. (1) can be derived:

$$d = -0.002 t + 2.0443. \quad (1)$$

The X-ray diffraction patterns of the cadmium and mercury doped lamellar silica samples are shown in Fig. 3. As can be observed, the doped samples presented three orders of 001 reflections, which confirmed the lamellar nature of the doped matrices. The diffraction peaks for 001, 002 and 003

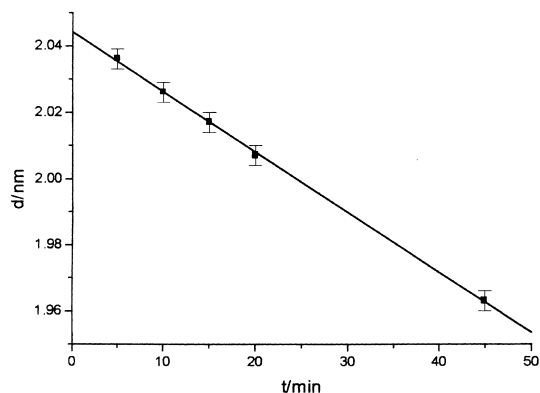


Fig. 2. Interlayer  $d$ -spacing values for 001 diffraction plane as function of time for 760 mPa pressed lamellar silica samples.

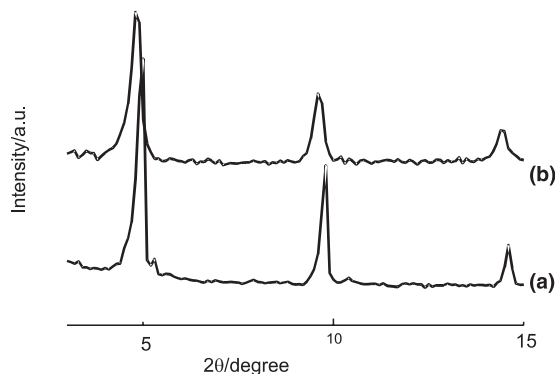


Fig. 3. X-ray diffraction patterns for 10.0 mmol metal doped lamellar silica sample with  $\text{CdCl}_2$  (a) and  $\text{HgCl}_2$  (b).

are located at 4.9, 9.7 and 14.6, and 4.8, 9.6 and 14.4 degrees for cadmium and mercury doped samples, respectively. The plots of lamellar distance for 001 diffraction plane as function of time,  $t$ , for samples pressed to 760 mPa are shown in Figs. 4 and 5, respectively. The coefficient of correlation  $r$  values are 0.9999 and 1.0000 for these two straight lines, respectively. For cadmium- and mercury-doped samples, the following can be derived:

$$d = -0.007 t + 1.917, \quad (2)$$

$$d = -0.001 t + 1.822. \quad (3)$$

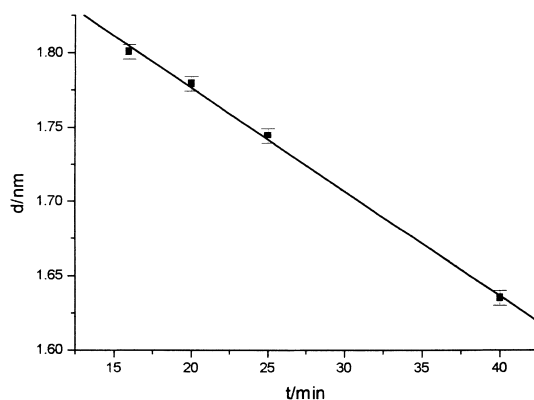


Fig. 4. Interlayer  $d$ -spacing values for 001 diffraction plane as function of time for 760 mPa pressed 10.0 mmol of cadmium-doped lamellar silica samples.

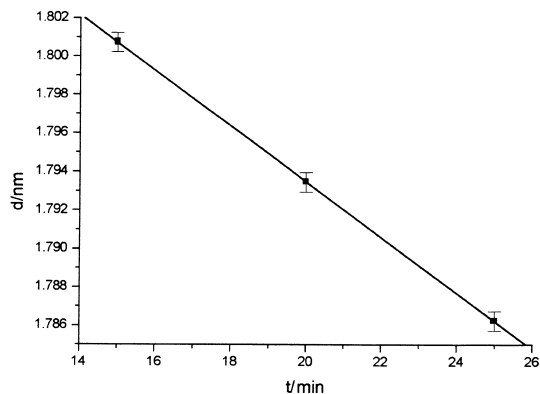


Fig. 5. Interlayer  $d$ -spacing values for 001 diffraction plane as function of time for 760 mPa pressed 10.0 mmol of mercury-doped lamellar silica samples.

#### 4. Discussion

An important feature to be considered in all these structures is related to the disposition of the *n*-dialkylamine molecules into the interlayer space. In the present case, a chain length of 1.15 nm was calculated for the amine bonded to the inorganic layers, by using covalent radii values for carbon, nitrogen and hydrogen atoms [16]. Based on this value, it can be inferred that two *n*-dialkylamines are bonded in opposite inorganic sheets, which basic amine centres are hydrogen bonded to the inorganic backbone, within the same lamellae. In this arrangement, one molecule is located above the other one in a linear structural conformation to produce the obtained interlayer space of 2.3 nm, as schematically represented in Fig. 6.

The silica pressed under 760 mPa for 45 min exhibited an interplanar distance of 1.96 nm, which number indicated a reduction of 16%, in comparison to the unpressed sample. The difference observed (0.36 nm) is almost one-third of the chain length of 1,12-diaminedodecane molecule. This interlamellar contraction is only possible if

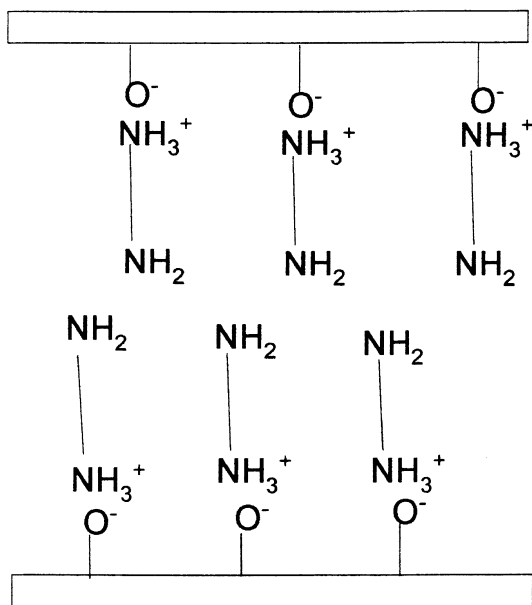


Fig. 6. Schematic representation of the orientation of the diamine chains in the interlayer space of the undoped lamellar silica samples.

the *n*-dialkylamine molecules adopted some kind of inclined conformation. This new rearrangement implied that the orientation of the alkyl-chains is not only determined by the charge density of the silica layer [1], but also is dependent on the external pressure. Thus, the thermodynamic stability of the intralamellar conformation of the diamine molecules was directly affected by the external pressure.

Based on the experimental results summarized in Figs. 2–4, at constant pressure, the interlayer distance is a function of time, expressing by  $d=f(t)$ . The fact that  $d$ -values gave a linear function with  $t$ , indicated that, for the three investigated samples, an equilibrium state characterized by the relationship,  $d=f(t)=\text{constant}$  was not established. Then, the required time to reach the equilibrium state is unknown.

The values derived from Eqs. (1)–(3) showed that the interlamellar distance for the cadmium-doped sample is more affected by an increase in the external pressure than mercury or undoped samples. These facts suggested that the interlamellar tridimensional framework for the mercury sample, formed with *n*-dialkylamine compounds, resulting from the coordination reaction gave a more rigid arrangement to the final structure.

From the coordination stereochemical point of view, cadmium can resemble zinc or mercury, depending on the number and the type of available ligands [17]. In comparing the X-ray diffraction patterns shown in Fig. 3, the results show that both elements exerted the same effect on the silica structure, under atmospheric pressure. Hence, it can be inferred that, under an increased pressure, cadmium can change its coordination environment, to adopt a most stable structure, which could be a final tetrahedral conformation for the cation within the lamellae.

Silica and metal-doped lamellar silica samples were pressed and the X-ray diffraction patterns were recorded after 1–5 days. In such experimental condition, the decrease in interlayer distance did not appear as a reversible phenomenon.

The heating effects on the structure of the pressed samples were not investigated. However, on heating, silica and metal-doped lamellar silica samples [18], as well as hexagonal mixed oxides

such as Ti–Zr [18] obtained by the neutral amine route, showed a release of the organic moiety, in temperatures ranging from 93°C to 250°C. Such kind of thermal degradation leads to structural transformations of the type: lamellar → hexagonal and hexagonal → amorphous [18,19]. Hence, any dynamic X-ray analysis of the samples under heating, must be performed in a temperature range, which avoids the release of organic moiety from the matrix.

### Acknowledgements

The authors thank CAPES-PICDT (R.F. de F.) and CNPq (C.A. and L.M.) for fellowships and FAPESP for financial support.

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