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Synthesis, Infrared and Powder X-Ray Diffraction Studies of Mixed Halogen Sodalites of the Type $Na_8[AlSiO_4]_6Cl_{2-X}I_X$ and $Na_{8-X}Ag_X[AlSiO_4]_6Cl_{0.52}I_{1.48}$

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The present work deals with the synthesis of mixed halogen sodalites of the type $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ that have been synthesized by using a low temperature hydrothermal technique. Infrared spectroscopy has been used for the confirmation of the framework structure. The structure of mixed halogen sodalite was established by X-ray Rietvelt refinement in the space group $P\bar{4}3n$. While, a silver containing derivatives, $Na_{8-x}Ag_x[AlSiO_4]_6Cl_{0.52}I_{1.48}$, obtained through aqueous ion exchange method. In the present study more emphasis is given to find out the correlation of Si-O-Al angle and unit cell parameter with concentration of iodide for different sodalites of $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ (where, $0 < x < 2$).

Key Words: Mixed sodalities, Hydrothermal method, Silver ion exchange, Zeolite-A.

INTRODUCTION

Halogen alumino-silicate sodalites of the type $M_8[AlSiO_4]_6X_2$, have cubic symmetry and crystallize in the space group $P\bar{4}3n$ [1,2]. The sodalite structure is a space-filling arrangement of identical cages having the form of truncated octahedra with inner diameter of *ca.* 6.5 Å. The alumino-silicate framework is made of regularly alternating tetrahedrally co-ordinated Al and Si atoms, which are connected through oxygen atoms. Each cage has six-eight atom rings and eight-twelve atom rings, containing four and six T-atoms, respectively.

Most of the work is available for the sodalite of the type[3-8] $M_8[AlSiO_4]_6X_2$, where, M is cation (Na^+, K^+, Ag^+, *etc.*) and X is an anion of the type Cl^-, Br^-, I^-, ClO_4^-, *etc.* Sodalites are currently of considerable interest, as a periodic matrices of quantum confined semiconductor clusters and cluster arrays[9] and since the sodalite cage is a polyhedral building

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unit of some important zeolites. The literature survey shows that little attention was given to the study of mixed halogen sodalites of the type $Na_8[AlSiO_4]_6Cl_{2-x}I_x$, apart from the work of Weller[10]. Hence the present work is undertaken for the systematic study of mixed Cl/I-SOD. The different sodalites are prepared by taking different compositions of chloride and iodide and the subsequent product was analyzed by infrared spectroscopy and powder X-ray diffraction. A relationship has been observed among IR absorption bands, the Al-O-Si angle and unit cell edge. Further, the present study also deals with the facile exchange[11] of silver from aqueous silver nitrate solution. The silver exchanged sodalites of general stoichiometry $Na_{8-x}Ag_x[AlSiO_4]_6Cl_{0.52}I_{1.48}$ have been studied in detail.

EXPERIMENTAL

A number of methods[12-15] are available for the synthesis of sodalites of the form $M_8[AlSiO_4]_6X_2$. Apart from these methods, we have modified the synthesis method for mixed halide sodalite by using Zeolite-A as a starting material. The $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalites (Cl/I-SOD) were synthesized in the range of $O < X < 2$ stoichiometry using hydrothermal technique. The appropriate mixture was taken in teflon bottle containing 20 mL of distilled water. This mixture was vigorously stirred to obtain optimum homogeneity. The reaction mixture was held at 100°C for 1 week. The product was recovered by filtration and rinsed with distilled water and dried overnight at 100°C.

Samples of different Cl/I ratio's were prepared by varying the concentrations of NaCl and NaI in the reaction mixture. The actual chloride and iodide stoichiometry was determined by using a potentiograph (Metrohm Herisau, E536). For this, an accurately weighed amount of sodalite was dissolved in 12 % HNO_3 to liberate the relevant anion in to solution. The stirred solution was then titrated with $AgNO_3$ standard solution. The sodalite framework has been well established by infrared spectroscopy. The unit cell size and Al-O-Si angle for all the samples were determined by using powder X-ray diffraction method.

While, the silver derivative of $Na_{8-x}Ag_x[AlSiO_4]_6Cl_{0.52}I_{1.48}$ was synthesized by hydrothermal process. In this method, the exchange of silver for sodium was achieved by an ion-exchange reaction using silver nitrate in a teflon bottle, containing sufficient water, at 100ºC for 1 week. Product stoichiometry was controlled by varying the $AgNO_3$ to parent sodalite ratio. The ion-exchange product was washed with water and dried at 100°C overnight. The subsequent changes in IR frequencies of the different modes of vibration are studied.

Infrared spectra in the range of 2000-300 cm^{-1} were measured as KBr pellets on a Perkin-Elmer 325 grating spectrophotometer.

RESULTS AND DISCUSSION

The observed IR frequencies in different region for various mixed sodalites are given in Table-1 along with reaction mixture stoichiometry and analyzed stoichiometry. Table-1 shows that the three kinds of IR frequencies are occurring[16,17] in the following regions: ν_{as} (Al-O-Si) (asymmetric stretching vibrations) 996-981 cm^{-1}, ν_s (Al-O-Si) (symmetric stretching vibrations) 735-660 cm^{-1}, δ (O-T-O) (bending vibration) 468-429 cm^{-1}.

TABLE-1
REACTION MIXTURE STOICHIOMETRY, ANALYZED STOICHIOMETRY AND IR FREQUENCIES (cm^{-1})

Reaction mixture stoichiometry	Analyzed stoichiometry	ν_{as}(Al-O-Si)	ν_s(Al-O-Si)	δ(O-T-O)
$Na_8[AlSiO_4]_6Cl_2$	$Na_8[AlSiO_4]_6Cl_2$	981	738,711,671	468,437
$Na_8[AlSiO_4]_6Cl_{0.6}I_{1.4}$	$Na_8[AlSiO_4]_6Cl_{1.4}I_{0.6}$	986	733,708,667	466,435
$Na_8[AlSiO_4]_6Cl_{0.5}I_{1.5}$	$Na_8[AlSiO_4]_6Cl_{1.02}I_{0.98}$	988	732,706,664	464,434
$Na_8[AlSiO_4]_6Cl_{0.56}I_{1.44}$	$Na_8[AlSiO_4]_6Cl_{0.95}I_{1.05}$	990	730,705,663	464,434
$Na_8[AlSiO_4]_6Cl_{0.5}I_{1.5}$	$Na_8[AlSiO_4]_6Cl_{0.74}I_{1.26}$	991	729,702,660	464,433
$Na_8[AlSiO_4]_6Cl_{0.45}I_{1.55}$	$Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$	993	729,703,662	463,432
$Na_8[AlSiO_4]_6I_2$	$Na_8[AlSiO_4]_6I_2$	996	726,700,660	456,429

A plot of iodide concentration in the feed *versus* product, for $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalite is shown in Fig. 1. It was observed that chloride is preferentially embedded in the sodalite cages. It is suggested that two general reasons are possible: (i) The stronger coulomb force exerted by the Cl^- on the Na^+ is responsible for the preferred formation of a cage containing Cl^- over I^-, (ii) The faster diffusion of Cl^- in aqueous solution dominates the synthesis.

The structure of NaCl-SOD was first solved by Pauling[1] in 1930. After Pauling's work, many people determined the structure of NaOH-SOD[18], KCl-SOD[19], $NaMnO_4$-SOD[20] as well as for nosean[21], laurite[22] and silica sodalite[23]. The crystal structure of Cl/I-SOD was established by powder X-ray Rietveld refinement. X-ray power data were collected in θ-θ geometry, using CuKα radiation for $10 < 2\theta < 93°$. The data analysis was carried out using the programmed GSAS. The framework structure of the sodium-chloride-aluminosilicate sodalite $Na_8[AlSiO_4]_6Cl_2$ was used as the starting model in space group $P\bar{4}3n$, assuming perfect silicon/aluminium alternation over the framework tetrahedral nodes. One of typical X-ray powder diffraction pattern is shown in Fig. 2.

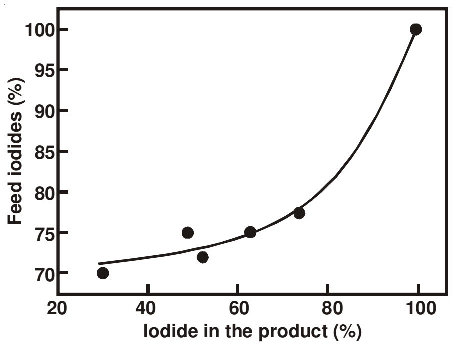

Fig. 1. Plot of iodide content of $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalite in the feed *versus* iodide in the product

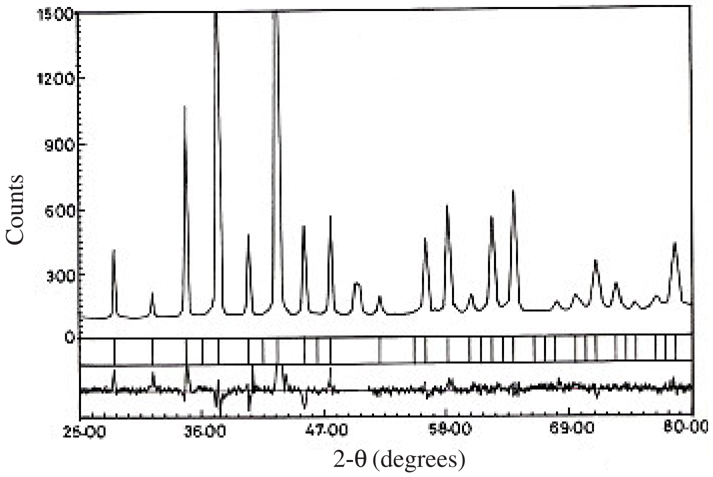

Fig. 2. Powder X-ray diffraction data for $Na_8[AlSiO_4]_6Cl_{1.02}I_{0.98}$, Full line is calculated profile, middle thick marks show the reflection position and lower continuous line is the difference plot

X-ray powder diffraction data were refined in the space group P43n with success for several samples of $Na_8[AlSiO_4]_6Cl_{2-x}I_x$. The refinement factors used are $R_p = \Sigma | y_o - Cy_c |/\Sigma y_o$ and $R_{wp} = [\Sigma w(y_o - Cy_c)^2/wy_o^2]^{1/2}$, C is a scale factor. In the present study our main interest is to find the correlation between the cell parameter and Si-O-Al angle as a function of iodide concentration in Cl/I-SOD. Table-2 shows the average values obtained for unit cell parameter and Si-O-Al angle for different mixed Cl/I-SOD.

Fig. 3A shows the plot of cell parameter as a function of iodide content in $Na_8[AlSiO_4]_6Cl_{2-x}I_x$. This figure also shows that, as iodide concentration increases, the cell parameter increases. The Si-O-Al angle appears to be an

TABLE-2
OBSERVED UNIT CELL PARAMETER AND Al-O-Si ANGLE FOR DIFFERENT MIXED HALIDE SODALITES

Sodalites	Cell parameter a, (Å)	Bond angle, Al-O-Si (º)
$Na_8[AlSiO_4]_6Cl_2$	8.8850	
$Na_8[AlSiO_4]_6Cl_{1.4}I_{0.6}$	8.9244	137.15
$Na_8[AlSiO_4]_6Cl_{1.02}I_{0.98}$	8.9543	138:41
$Na_8[AlSiO_4]_6Cl_{0.95}I_{1.05}$	8.9671	138:41
$Na_8[AlSiO_4]_6Cl_{0.74}I_{1.26}$	8.9772	139.12
$Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$	8.9911	140.12
$Na_8[AlSiO_4]_6I_2$	9.0181	141.76

almost linear function of the cell constant (Fig. 3B). This is accounted for compositional flexibility which exists within the sodalite family, where changes in the nature of cage species are accommodated by variation in the Si-O-Al angle. The flexibility in case of mixed sodalite series is due to Cl^-, I^- and it results in the expansion of Si-O-Al angle and hence the cage size for trapping the large halide.

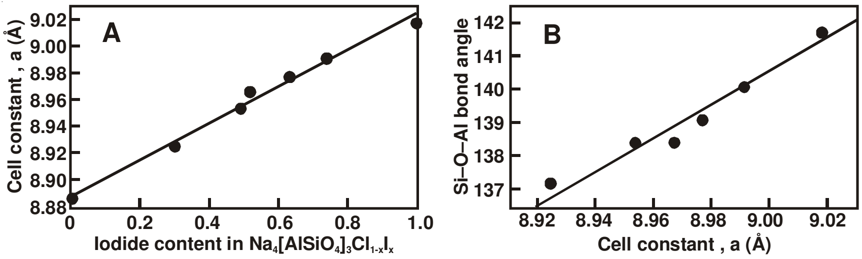

Fig.3. Correlation between (A) Cell constant (a) and iodide content, (B) Si-O-Al angle and cell constant for $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalite series

Further, for all mixed halogen sodalites, refinement was achieved with sodium on a single site (x,x,x) showing all materials consisting of mixture of chloride, iodide and sodium satisfying Na-Cl and Na-I coordination geometry. The movement Na^+ ion away from the cage center is observed as more iodide is incorporated (Table-3).

Fig. 4A and B shows the variation of Na position and Na-X distance with iodide content in $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalites. Fig. 4 also shows that the Na-X distance increases almost linearly with I^- content. This can be easily, explained by taking the geometric average of the NaCl and NaI distance for the specific stoichiometry.

TABLE-3
CALCULATED Na-POSITION AND Na-X DISTANCE FOR MIXED HALOGEN SODALITES

Sodalite	Na-Position	Na-X Distance
$Na_8[AlSiO_4]_6Cl_{1.4}I_{0.6}$	0.1890	2.922
$Na_8[AlSiO_4]_6Cl_{1.02}I_{0.98}$	0.1894	2.937
$Na_8[AlSiO_4]_6Cl_{0.95}I_{1.05}$	0.1905	2.959
$Na_8[AlSiO_4]_6Cl_{0.74}I_{1.26}$	0.1911	2.985
$Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$	0.1955	3.045
$Na_8[AlSiO_4]_6I_2$	0.2025	3.156

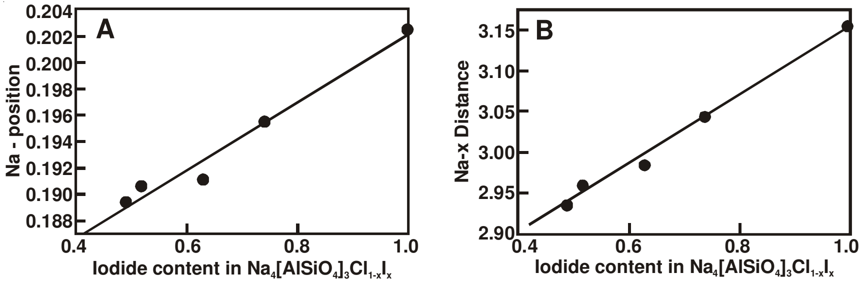

Fig. 4. Relation between (A) Na-position and (B) Nax distance for $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalite series

This shift in the wavelength of the stretching and bending vibration as a function of the unit cell parameter is shown in Fig. 5. The shift to be longer wavelength for ν_{as} is accounted on the basis of an increase in the Si-O-Al angle with unit cell parameter. This is in agreement with the plot of Si-O-Al angle *vs.* unit cell parameter (Fig. 3B).

Silver derivatives of $Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$ sodalites

In the present work we have studied the silver exchange of $Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$ sodalite, which was carried out by taking appropriate proportions of silver nitrate solution and sodalite. The frequencies observed for these sodalites, in the infrared spectrum for successive Ag-exchange are given in Table-4.

The asymmetric stretching vibration, ν_{as}, only shows slight decrease with silver exchange, whereas in the region of ν_s and δ-vibrations, the shift of bands to lower frequency with increasing silver content is rather pronounced (Fig. 6). The silver halide sodalites have a slightly smaller cell constant than the corresponding sodium sodalite[24]. This is due to the decrease of the cation-halide bond distance.

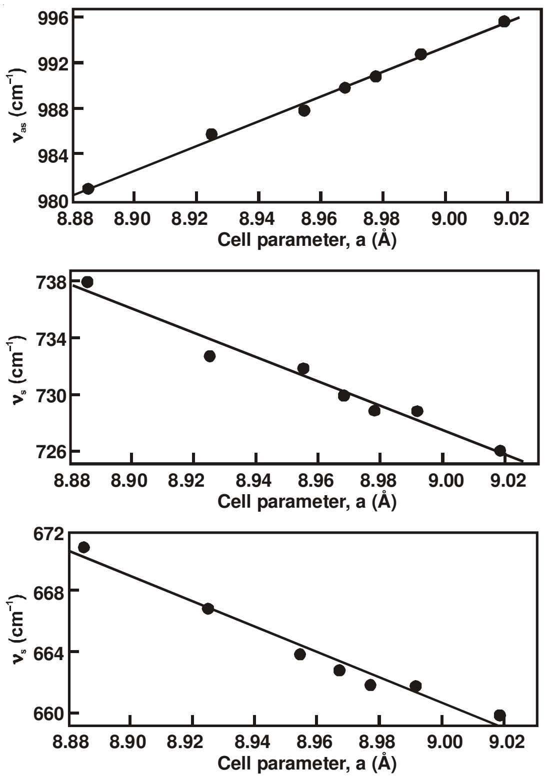

Fig. 5. Plot of frame work vibrational frequency *vs.* cell dimensions for $Na_8[AlSiO_4]_6Cl_{2-x}I_x$ sodalite series

TABLE-4
IR FREQUENCIES (cm^{-1}) OF DIFFERENT SAMPLES OF AMOUNT OF SILVER EXCHANGED IN $Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$ SODALITE

Reaction mixture stoichiometry	ν_{as}(Al-O-Si)	ν_s(Al-O-Si)	δ(O-T-O)
$Na_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$	993	729,702,661	462,432
$Ag_2Na_6[AlSiO_4]_6Cl_{0.52}I_{1.48}$	987	426,701,660	461,431
$Ag_4Na_4[AlSiO_4]_6Cl_{0.52}I_{1.48}$	987	724,699,659	460,430
$Ag_6Na_2[AlSiO_4]_6Cl_{0.52}I_{1.48}$	987	720,—,657	458,429
$Ag_8[AlSiO_4]_6Cl_{0.52}I_{1.48}$	987	717,—,656	458,427

For example in the present case of iodide sodalite the cell edge of the sodium form is 9.008 Å and we have found a reduction to 8.968 Å for $Ag_8[AlSiO_4]_6I_2$ which is in good agreement with the value reported in the literature[24]. This reduction in the cell edge should result in an increase of ν_{as} and δ by about 3 cm^{-1} and the decrease of 2 cm^{-1} for ν_{as}. These values results from the correlation found for the frequencies with the cubic cell edge[14].

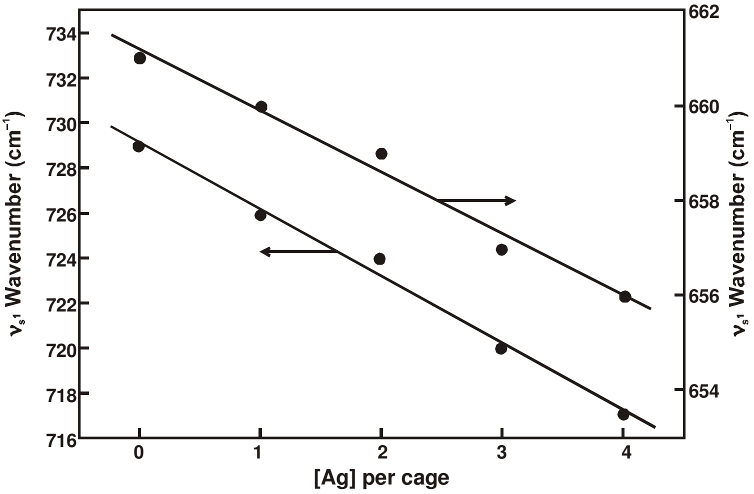

Fig. 6. Dependence of two *vs.* stretching in $Na_4Ag_x[AlSiO_4]_6Cl_{0.26}I_{0.74}$ sodalite with various degree of silver exchange

The silver sodalites seems not to fit into this correlation since a reduction for ν_s and δ is observed and also ν_{as} is decreased by a larger amount than would be expected from the cell edge correlation.

One possible explanation for this is that, in these silver sodalites the Al-O and Si-O distances and also the Al-O-Si angles are considerably modified compared with other sodalites. Since these distances and the Al-O-Si angles are thought to be very important for the actually observed frequencies[14] this could be an explanation for the observed frequency shift.

The Al-O and Si-O distances and the Al-O-Si angles are considerably altered in Ag-halogen sodalites come from the structure reported by Stein *et al.*[24]. Nevertheless we have refined the structure of $Ag_8[AlSiO_4]_6I_2$ by Rietveld refinement and could not confirm this large deviation. The structure is very consistent with the structure model proposed by Hassan and Grundy[25].

The reason for the shift to lower frequencies comes from the specific interaction of the Ag^+ with the framework oxygen's. This frequency shift is also observed in silver salts with complex oxo-anions compared with the isomorphous alkali-salts[26,27], which may be due to the Ag^+ forms partly covalent bonds with the oxygen and thus weakens the Al-O- and Si-O-bonds considerably which has already been observed in various salts with complex oxo-anions[27,28].

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REFERENCES

1. L. Pauling, *Z. Kristallogr.*, **74**, 213 (1930).
2. W. Depmeier, *Z. Kristallogr.*, **199**, 75 (1992).
3. J.C. Buhl and J. Lons, *Alloys Comp.*, **235**, 41 (1996).
4. Th. Veit, J.C. Buhl and W. Hoffman, *Catalysis Today*, **8**, 405 (1991).
5. R.M. Barrer and D.E.W. Vaughan, *J. Phys. Chem. Solids*, **32**, 731 (1970).
6. J. Felsche and S. Luger, *Ber. Bunsenges. Physik. Chem.*, **90**, 736 (1986).
7. I. Hassan and H.D. Grundy, *Acta Cryst.*, **C39**, 3 (1983).
8. A. Stein, G.A. Ozin, P.M. Macdonald, G.D. Stucky and R. Jelinek, *J. Am. Chem. Soc.*, **114**, 5171 (1992).
9. G.A. Ozin and G.D. Stucky, *J. Am. Chem. Soc.*, **114**, 8119 (1992).
10. M.T. Weller and W. Wang, *Eur. J. Solid State Inorg. Chem.*, **26**, 619 (1989).
11. R.M. Barrer and J.S. Raitt, *J. Chem. Soc.*, 4641 (1994).
12. E. Engelhart, L. Felsche and P. Siegre, *J. Am. Chem. Soc.*, **114**, 1173 (1992).
13. D.J. Schipper, Z. Van Doome and P.T. Bolwijn, *J. Am. Chem. Soc.*, **55**, 256 (1971).
14. C.M.B. Hendersone and D. Taylor, *Spectrochim. Acta*, **33A**, 283 (1977).
15. J.C. Buhl, *Mat. Res. Bull*, **28**, 1319 (1993).
16. L. Godber and G.A. Ozin, *J. Phys. Chem.*, **92**, 243 (1988).
17. E.M. Flanigen and H. Khatarni, *Adv. Chem. Series*, **101**, 201 (1971).
18. S. Luger, J. Felsche and P. Fischer, *Act. Cryst.*, **C43**, 1 (1987).
19. B. Beagley, C.M.B. Henderson and Taylor, *Mineral Mag.*, **56**, 459 (1982).
20. V.I. Sardanov, W.T.A. Harrison, T.E. Gier, G.D. Stucky, A. Popitsch, K. Gatterer, D. Markgraber and H.P. Fritzer, *J. Phys. Chem.*, **98**, 4673 (1994).
21. I. Hassan and H.D. Grundy, *Can. Mineral*, **27**, 165 (1989).
22. I. Hassan, R.C. Peterson and H.D. Grundy, *Acta Cryst.*, **C4I**, 1985 (1985).
23. J.W. Richardson, J.I. Pluth, J.Y. Smith, W.J. Dytrych and D.M. Bibby, *J. Phys. Chem.*, **92**, 243 (1988).
24. A. Stein, G.A. Ozin, P.M. Macdonald, G.D. Stucky and R. Jelinek, *J. Am. Chem. Soc.*, **114**, 5171 (1992).
25. I. Hassan and H.D. Grundy, *Act. Cryst.*, **B40**, 6 (1984).
26. E.I. Baran, P.I. Aymonino and A. Muller, *Z. Naturforsch.*, **21b**, 271 (1969).
27. A. Muller, E.J. Baran and R.D. Carter, *Struct. Bonding*, **26**, 81 (1976).

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