

## 22.3-5 THREEDIMENSIONAL ANALYSIS OF VITREOUS SILICA BY THE PARACRYSTAL CONCEPT.

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The combined interpretation of the X-ray intensity distribution of vitreous silica, its autocorrelation function and a rotatory distorted model of the high cristobalite symmetry  $Fd\bar{3}m$  for the first time yields a three-dimensional solution of this paracrystalline structure. A  $17^\circ$ -twist of adjacent  $\text{SiO}_2$ -motives clock- and counterclockwise around one cell axis bends the tetrahedral angles by  $+17^\circ$  and  $-3^\circ$  and Si-O-Si-angles by  $35^\circ$ . The calculated convolution product of this arrangement leads to a radial density function, which is in good agreement with the reduced radial density function, derived from the intensity plot of R.L. Mozzi and B.E. Warren (J. Appl. Cryst. (1969), 2, 164). The stressed chemical bonds cause the bearing (111)-netplanes to perform a standard deviation  $g = 10\%$  of their mean distance  $d_{111} = 4,15 \text{ \AA}$ , as determined by the unfolded prominent reflection. The known hexahedral rings of Si-atoms combine to form a spatial network within paracrystals of octahedral shape consisting of  $N+1 = 4$  (111)-netplanes. These define their boundary surfaces of a roughness  $\alpha^2 = \sqrt{N} \cdot g = 0,17$ . The calculated structure factor and the atomic scattering factors combine well in order to fit the measured intensity of the X-ray diffraction.

22.3-6 A QUASI-CRYSTALLINE SIMULATION OF "Pb<sub>2</sub>M<sub>t</sub><sup>II</sup>M<sub>t</sub><sup>III</sup>F<sub>9</sub>" FLUORIDE GLASSES STRUCTURE. by A. Le Bail,

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Interference functions (neutrons, X-ray) and RDF of a serie of isomorphous substituted glasses "Pb<sub>2</sub>M<sub>t</sub><sup>II</sup>M<sub>t</sub><sup>III</sup>F<sub>9</sub>" ( $M_t^{\text{II}} = \text{Mn}^{2+}, \text{Zn}^{2+}$ ;  $M_t^{\text{III}} = \text{Fe}^{3+}, \text{V}^{3+}, \text{Ga}^{3+}$ ) have been simulated using a new "quasi-crystalline" method. The procedure is based on the well known equations used in X-ray line profile analysis of imperfect crystals (B.E. WARREN, X-ray Diffraction, Addison-Wesley Pub., 1969) where of course only the broadening due to strain is considered (and not small coherent domains). The choice of a Gaussian strain distribution and of a deformation increasing as the square of the distance leads to a gaussian peak-shape varying in halfwidth for each reflexion hkl of a simulated powder pattern. Good results are obtained with structural models like  $\text{BaFe}_5$  or

$\text{Ba}_2\text{CoFeF}_9$ -type which confirm previous interpretations in terms of corner-sharing  $M_t F_6$  octahedra and close packing of large ions  $F^-$  and  $\text{Pb}^{2+}$  for the glasses. The number of parameters needed for a simulation is the same as for a crystalline structure with only two additional one's relative to strain, so that it is believed that this method could be used as a basis for structural refinement of the model in cases where several interference functions with large variations are known (isotope and isomorph substitution experiments). Tests are actually made on our data in this direction.

## 22.3-7 LARGE-ANGLE X-RAY SCATTERING STUDY OF AMORPHOUS METALLIC COMPLEXES OF DITHIOXAMIDE

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Dithiooxamide (rubeanic acid) is known to give metallic complexes with remarkable electric, magnetic and catalytic properties. Spectroscopic studies, especially on nickel and copper complexes, raised up conflicting hypothesis about the ligand coordination scheme.

In order to correlate the physical properties with the structural order, we have prepared and studied, by the LAXS method, two amorphous complexes:  $\text{CuL}(\text{H}_2\text{O})$  and  $\text{Ni}_4\text{L}_5(\text{H}_2\text{O})_{0,25}$  (L = dithiooxamide).

The two compounds have essentially the same local structure as it can be seen on the radial distribution functions  $F(r)$  (Fig. 1).

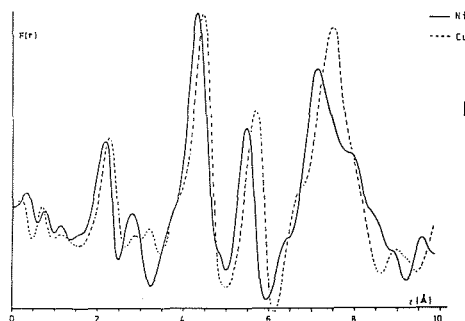


Fig. 1

The shift on the peak positions ( $\approx 0.2 \text{ \AA}$ ) is due to the variation of coordination bond lengths. The difference in peak intensities are correlated to the chain length. So a structural model has only been designed for the Ni complex.

This model corresponds to the theoretical RDF in figure 2 and can be described by the following features:

- the ligand is in trans conformation and planar.
- The coordination is ensured by the four donor atoms (S,N) and the Ni environment is square planar.
- The ribbons, thus formed, stack perpendicularly to the ligand plane with an interval equal to  $3.6 \text{ \AA}$ .
- This very high symmetry of the model must be attenuated by a kind of variability in the local structure (small variations in bond lengths and angles -small deviations to the ligand planeity and to the stacking interval-...) to explain the amorphous nature of the studied materials.

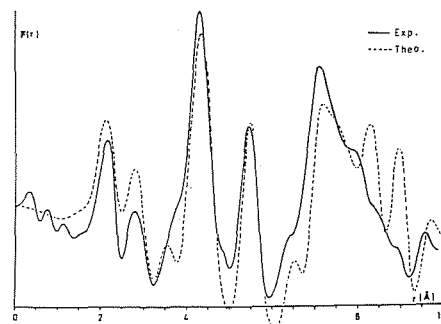


Fig. 2