

22.3-2 STRUCTURE OF $\text{MOO}_3\text{-P}_2\text{O}_5$ GLASS SYSTEM. BY A. K. NANDI & B. MUKHERJEE
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The radial distribution function (rdf) of $\text{MOO}_3\text{-P}_2\text{O}_5$ glass system with the use of dopants and without have been determined from x-ray diffraction. The rdf peaks are assigned as corresponding to P-O, MO-O, $(\text{O-O})_P$ and $(\text{O-O})_{MO}$ distances. Correspondingly the coordination numbers under the peaks have also been determined. On the basis of the rdf studies the authors infer the glass structure of the compounds as corresponding to tetrahedral configuration for both the cations and there are a certain number of non-bridged Oxygen ions which are mutually arranged in tetrahedral configuration around unoccupied holes. The Oxygen tetrahedra are sharing only corners and not edges or faces. The use of 5% dopants (Mn^{2+} or Co^{2+}) replacing MO^{6+} leads to a more unfolded type of structures.

22.3-3 X-RAY DIFFRACTION STUDIES OF GLASSY As_2S_3 AND ITS AG ALLOYS. BY MOSTAFA RADWAN,
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X-ray diffraction; radial distribution studies of glassy $\text{Ag}_x(\text{As}_{0.4}\text{S}_{0.6})_{100-x}$ alloys, with $0 \leq x \leq 25$ have been performed. The studies suggest that glassy As_2S_3 and its low concentration Ag alloys have an atomic arrangement close to that of crystalline As_2S_3 (Orpiment structure), while large regions of the glassy alloys with higher Ag percentage have an atomic arrangement close to that of crystalline Ag As_2S_3 . The alloy radial distribution function results indicate that the average nearest neighbor coordination number increases from 2.61 for $x=0$ to 4.2 for $x=25$ which could rationalize the electrical conductivity change.

22.3-4 Ultrastructural and Analytical Studies of Amorphous Calcium Phosphates, Pyrophosphates and Phosphate-Pyrophosphate Complexes. P.-T. Cheng, M.D. Grynbas and K.P.H. Pritzker; Mount Sinai Hospital University of Toronto, Toronto, Canada.

Amorphous calcium phosphate (ACP) is a long standing controversial subject in biomineralization processes, especially new bone formation. Although Grynbas et al. (J. Mat. Sci. 19:723, 1984) have shown by x-ray diffraction radial distribution function (RDF) that there is no detectable amount of ACP in either embryonic or mature bone (<1%), the possible role of ACP as a labile intermediate transforming rapidly into impure poorly crystalline calcium apatite as found in bones cannot be ruled out. Moreover ACP has been suggested to be present in intracellular and extracellular (in lower species only) calcium deposits suggesting that ACP may be stabilized by some ambient agents including Mg^{++} , pyrophosphate (PPI) and glycosaminoglycans.

PPI has been found by Cheng and Pritzker (J. Rheumatol. 10:769, 1983) to be especially potent in inhibiting the ACP-apatite transformation. Also Mg^{++} ions inhibit this transformation by competing with Ca^{++} and retarding crystallization. In a set of solutions containing orthophosphate (Pi) and PPI as well as Ca^{++} , Mg^{++} , Na^+ , Cl^- in concentrations similar to in vivo values, the stable solid products formed were (A) mixtures of monoclinic and triclinic calcium pyrophosphate dihydrate crystals [CPPD (M+T)], (B) precipitates amorphous to x-ray diffraction, (C) calcium apatite crystals, depending on the solution Pi/PPI values: 3, 3-100, >100 respectively. This predicts calcium apatite bone in a high Pi/PPI environment and calcified articular cartilage and intervertebral discs form CPPD (M+T) crystals in a low Pi/PPI environment.

When studied by transmission electron microscopy, precipitates (B) do not give any crystalline forms nor electron diffraction patterns. Precipitates (B) when air-dried show morphology consisting of spheroids with electron lucent centers (Fig. 1) similar to that of ACP as reported by Weber et al. (Arch. Biochem. 120:723, 1967). However, when dehydrated through graded alcohols, they show a very different morphology consisting of extremely fine particles with diameters as small as 1 nm (Fig. 2), suggesting that precipitates (B) are truly amorphous. However, the confirmation of the amorphous structure of precipitates (B) awaits our RDF studies now being undertaken.

Precipitates (B) have been tentatively assigned to be ACP, amorphous calcium pyrophosphate (ACPP), amorphous calcium pyrophosphate-phosphate complexes (ACPP-P) according to their Ca/P ratios (close to 1.5, close to 1.0, in between, respectively) which vary with Pi/PPI values. However, spectroscopic and chemical studies are underway to quantitate the amounts of Ca^{++} , Mg^{++} , Pi and PPI in the three groups.

While both intra- and extracellular ionic Ca^{++} concentrations in vivo are highly regulated, those of Mg^{++} , PPI, and Pi are subject to wide fluctuations. As the solid phase formation is closely related to the ambient ion concentrations, the clarification of the interrelationships of crystalline and amorphous calcium phosphates and pyrophosphates, Ca/P and Pi/PPI ratios and other physical chemical parameters will provide insight into the conditions in which physiologic and pathologic calcifications form.

