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Differential thermal analysis of some irradiated materials: discussion

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Based on an excellent differential thermal analysis and X-ray powder diffraction study of radiation damage effects on the structures of ZrO_2, U_3O_8, and Al_2O_3, Berman (1978) has proposed that irradiated, amorphous U_3O_8 and Al_2O_3 are supercooled liquids (*i.e.*, true glasses). Berman also suggests that metamict minerals may be true glasses. While Berman's technique of studying radiation damage (DTA and powder diffraction of material which has been severely damaged by fission fragments) is of obvious value, we do not agree entirely with his conclusions concerning the nature of the radiation-damaged Al_2O_3 and the metamict state. The purpose of this note is to review evidence that metamict minerals may not be true glasses and to offer an alternative and equally plausible interpretation of the data presented by Berman.

Properties of the metamict state have been reviewed by Pabst (1952) and more recently by Ewing and Haaker (1979). Metamict minerals are a class of radioactive materials which were initially crystalline but which have become amorphous because of structural damage from alpha particles and recoil nuclei. Metamict minerals and glasses have a number of common properties. They (1) are optically isotropic, (2) lack cleavage and usually exhibit conchoidal fracture, (3) are amorphous to X-rays, and (4) form crystalline phases on heating.

Although metamict minerals have been studied extensively, little is known about the structure of the metamict state, since most studies have been concerned with identification after heat treatment (Lima-de-Faria, 1964). Differential thermal analysis and X-ray diffraction analysis of annealed material have been the most common methods of analysis of the metamict state (Kurath, 1957). There has only been a limited effort to use high-angle X-ray scattering techniques to examine the structure of the metamict state (Alexandrov and Pyatenko, 1959). Similarly there have been few electron diffraction studies of metamict minerals (Bursill and McLaren, 1966). Thus, information on the structure of the metamict state is sparse.

Part of the confusion about the structure of the metamict state and the fission-damaged amorphous state of irradiated Al_2O_3 may be due to the limitations of X-ray diffraction. X-ray powder diffraction is not useful in distinguishing between a true glass, with a random three-dimensional network (Zachariasen, 1932), and a crystalline material whose mean crystallite size is small. The width of X-ray diffraction maxima are a function of the mean crystallite size. As the mean crystallite size decreases below approximately 0.2 μm, broadening of diffraction maxima becomes progressively more severe. Materials with a mean crystallite size of approximately 0.01 μm fail to yield a recognizable diffraction pattern. If amorphous fission-damaged Al_2O_3 and metamict minerals are crystalline with a mean crystallite size of about 0.01 μm, then their X-ray diffraction patterns would be indistinguishable from those of a true glass.

Since relatively sharp electron diffraction patterns can be obtained on samples having a mean crystallite size of approximately 0.01 μm, it is a more useful technique than X-ray diffraction as a means to establish whether or not a material is a true glass or crystalline on a submicroscopic scale. Bursill and McLaren (1966) have applied transmission electron microscopy to the study of metamict and nonmetamict zircon. When flakes of these metamict zircons were examined by TEM, diffraction patterns revealed that they were composed of slightly misoriented zircon crystallites about 0.01 μm in diameter. Thus, in this instance, metamict zircon does not appear to be a glass. This observation is in basic agreement with the domain structure theory for metamict niobium tantalum oxide minerals as proposed by Graham and Thornber (1974).

The differential thermal analysis data of Berman (1978) do not necessarily support the contention that fission-damaged Al_2O_3 is a true glass. Berman reports that restoration of the crystalline structure is accompanied by an enthalpy change of 1.84 to 6 kcal/mole, whereas the heat of fusion of Al_2O_3 is approximately 26 kcal/mole. If fission-damaged Al_2O_3 is a true glass, then the energy change during annealing should be comparable to the heat of fusion. If 6 kcal/mole is an accurate measure of the enthalpy change associated with restoration of crystalline structure, then it is possible that fission-damaged Al_2O_3 is, instead of a glass, a highly disordered material which is similar in crystalline state to the metamict zircons studied by Bursill and McLaren (1966). The data of Berman (1978) are in agreement with similar studies already in the radiation damage literature, but the DTA and diffraction data do not preclude the possibility that fission-damaged Al_2O_3 is nonvitreous.

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