

Irradiated and metamict materials: relevance to radioactive waste science

RUSTUM ROY, E. R. VANCE

*Materials Research Laboratory, The Pennsylvania State University,
University Park, PA 16802, USA*

The relation of the structures of metamict mineral phases and non-crystalline solids is discussed; the question of radiation effects in solidified nuclear waste forms is considered in this regard. In ceramics, if the actinides can be concentrated in radiation-resistant phases such as uraninite or monazite, the overall radiation effects on the ceramics should be quite small.

1. Introduction

The relation of the structures of non-crystalline solids (NCS) to those of metamict mineral phases has been recently discussed [1]. It is attempted in the work reported here to clarify that relationship and to treat the role of metamictization in solidified nuclear waste forms.

Haaker and Ewing [1], in discussing a paper by Berman [2], have argued that metamict minerals should not be considered to be the same as "true glasses". (For the purpose of this work we will use here the working definition that a metamict mineral is one which shows no discrete spots on a Laue back-reflection X-ray pattern, or discrete rings on a powder photograph.) Haaker and Ewing [1] have gone on to generalize regarding the differences between such metamict phases and "true glasses" on the basis of alleged similarities between the ΔH_{fusion} values and the ΔH_{cryst} values of these materials (where ΔH_{fusion} and ΔH_{cryst} are the enthalpies of fusion and crystallization, respectively).

This generalization will be examined below. As an aside, Haaker and Ewing [1], apparently following Bursill and McLaren [3], erroneously attributed discrete spots in the electron diffraction patterns of metamict zircons to microcrystallinity supposedly not discernible by X-ray diffraction. We believe this to be an artifact of the Laue back-reflection geometry *vis-à-vis* the transmission electron diffraction experiment (see also [4]). As an illustration (a detailed geometrical discussion of the problem would be lengthy and, in our

opinion, out of place in the present communication) of the effect of geometrical factors, precession photographs taken with short wavelength (Mo) X-rays incident on zircons which were essentially metamict according to the above definition showed reasonably well-defined diffraction spots [5]. Both the X-ray precession and the electron diffraction experiments provide basically undistorted maps of the reciprocal lattice via the use of monochromatic radiation, unlike the Laue experiment.

2. Structure of non-crystalline solids

Solid-state science has been seriously confused by the paradigm of periodicity, and in some earlier papers [6-9] it was argued that the understanding of aperiodic structures has been neglected and warped by it. The structures of "solids" were determined for a large number of at first simple and later complex crystalline solids. Non-crystalline solids, however, could not be easily studied from a structural point of view and certainly could not easily be differentiated and classified. Hence they were grouped together as though they were all of the same structure; so was born the absurd usage "*the* structure of glass". In the same way as there are thousands of crystalline arrangements of atoms and ions, there is literally an infinity of different NCS structures. This latter larger number is to be expected since the periodicity condition is removed.

The reason for the confusion in the literature is that since we cannot easily determine, or

describe, the structure of each NCS, because our tools are inadequate, there is no obvious scheme under which to categorize NCS. It was for this reason that a "genetic classification" of NCS was proposed: Fig. 1, in [8], is directly relevant to this issue. It will be seen that the term "glass" is limited to that family of solid phases ($S, S', S'' \dots$) which are non-crystalline and derived from a liquid (L) phase of the same composition. Haaker and Ewing [1] agreed with these percepts in implying that a $S \rightarrow S'$ derived NCS, such as a metamict mineral, will probably not have the same structure as any $L \rightarrow S$ derived "true glass" (or other glass).

In general, one can expect something closer to a Prins "microcrystalline" model for a $S \rightarrow S'$ derived metamict mineral, as Haaker and Ewing [1] imply, although they did not explicitly mention the Prins school of glass structure. However, the very idea of microcrystalline fragments was first developed to describe the structure of "true glasses". Indeed, quite recently, Konner and Karle [10] proposed a model of SiO_2 -glass based on 10–20 Å-sized units of tridymite. Although the details of that proposal have been criticized [11], recent Raman spectroscopic studies of simple alkali-silicate glasses indicate the presence of different discrete "volumes" some of which are essentially crystalline [12]. Many structural and other properties of the ($L \rightarrow S$) glasses referred to above can best be explained by the non-homogeneous structural model [9]. This model, which is similar to that of Moriya [13], has as its central feature that, in most NCS, there are regions of different structure, each present as "micro-phases", with characteristic sizes of between 10 and 100 Å.

For radiation-amorphized solids, however, there are few data from which to draw conclusions, mainly because bulk specimens of only a very few solids have been rendered X-ray amorphous by irradiation in the laboratory: SiO_2 [14–16], diamond [17], ZrSiO_4 [18, 19], U_3O_8 [2, 18], and Al_2O_3 [2, 18]. Gaskell and Johnson [20] conclude that there is evidence for crystalline regions in both SiO_2 -glass and the neutron-damage-saturated material. Naguib and Kelly [21] have discussed other materials which can be rendered amorphous by ion implantation, but here there are complications with substrate epitaxy, preferential volatilization of constituent ions and with the use of thin films as starting materials.

3. Structure, metastability and reactivity of metamict phases

There has been a resurgence of interest in metamictization of minerals because of the possible relevance of this information to radioactive waste storage. Contrary to popular misconception, to date, in the U.S., virtually all actual hot solidification of radioactive waste which has been accomplished (CsCl and SrF_2 at Hanford, and calcines at Idaho) and 100% of all final disposal (assorted cement phases at Oak Ridge) has been in crystalline phases. So far little research and much engineering has been devoted to future plans to make a non-crystalline, glassy, waste form. We are therefore concerned with the possible effects of radiation on the structure, thermodynamics and kinetics of crystalline phases which may be partly or wholly metamictized (i.e. rendered non-crystalline).

Very small changes in the structure of crystalline phases can be studied by X-ray diffraction techniques and, in insulators, even more sensitive investigation may be undertaken using spectroscopic techniques. In the disordered structures of glasses, it is of course difficult to measure the structural changes that occur; change in dimensional and electrical properties can be studied. In crystalline phases, there might be phase changes or effects on the kinetics of phase changes. Roy and Buhsmer [22, 23] showed that fast neutron irradiation significantly altered the kinetics and temperature of the phase changes in various crystalline SiO_2 phases, Ca_2SiO_4 , and PbO . They showed, in effect, that radiation damage acted like negative pressure; the transition temperatures were displaced rather than smeared-out. Exposure to radiation results in the formation of a series of crystalline 'polymorphs' ($S \rightarrow S' \rightarrow S'' \dots$) usually with increasing molar volume. Vance and Boland [19] also commented on radiation damage apparently affecting the decomposition reaction of zircon.

The sensitivity of refractory crystalline materials to radiation varies greatly, although there is some suggestion that whether or not the structure is cubic is important [18, 21, 24]. "Open" structures, with "holes" or "channels" should promote location of displaced cations in metastable interstitial sites, rather than interstitial–vacancy recombination [25], although it has been argued that such a condition would not be sufficient for metamictization [26]. A further con-

dition must be met, namely, the rapid crystallization temperature, T_x , [27] must be well above room temperature, i.e., NCS formation in principle is not enough, it must be retained at the temperature of observation. It has also been commented that covalent bonding, rather than ionic bonding, promotes radiation sensitivity [21, 24]. High bond strength is of course directly correlated with T_x .

4. Radiation-induced property changes relevant to radiation waste sciences

For radioactive waste management, characterization of structure changes in the waste form as a result of self-irradiation damage is of interest, but other information is required. Over a period of 10^6 years, a high-level waste form (assumed to be intact) will experience an α -radiation dose of up to $\sim 10^{20} \alpha \text{ cm}^{-3}$ [28]. It is generally expected that α -recoil damage will be the prime contributor to radiation effects in solidified nuclear wastes. Although it has been suggested [29, 30] that β - and γ -radiation damage effects arising from radiolysis (as distinct from direct displacements) of silicates could be comparable to those arising from α -recoils, the radiolysis experiments are carried out at very high electron fluxes and the relation of these experiments to possible β -damage or γ -damage effects in a waste form is not clear at this stage. Also, the presence of H_2O and OH^- impurities may be significant [30, 31].

From accelerated ^{244}Cm doping tests [32], the density change of a high-level waste glass would be of the order of 1% after a dose equivalent to that encountered during storage for $\sim 10^6$ years, and it seems reasonable to assume that, for a ceramic formulation, the effects would be no greater if the actinides were concentrated in such radiation resistant phases as fluorite-structured UO_2 [18, 23] or monazite-type [33] phases. Differential density changes in a multiphase-containing waste need of course to be minimized to prevent microcracking and an increased tendency for stress corrosion.

However, by far the most important properties of the glass or ceramic waste form are those of general reactivity and solubility or "leachability" in various possible groundwaters, and on these questions little actual evidence exists, apart from the obvious fact that the very existence of metamict minerals implies that the damage does not render them *very* soluble or differentially leached.

In this regard, Mumpton and Roy [25] hydrothermally treated a number of metamict zircons

and, whereas only zircon was recrystallized in most cases, there was in a minority of cases some ZrO_2 formed in addition to the zircon. In these cases, it is possible that some SiO_2 had been preferentially leached out of the metamict zircon by groundwater. In the same vein, Haaker and Ewing [34] mention that annealing metamict zircons at 1000°C often produces ZrO_2 (with or without zircon) in the diffraction patterns; however, annealing such zircons at higher temperatures can remove the ZrO_2 and promote diffraction due to recrystallized zircon ([9], for example). All these differences are actually the result of crystallization kinetics in all such systems, as the voluminous literature on the phase diagram for $\text{ZrO}_2\text{-SiO}_2$ shows.

Haaker and Ewing [34] remark, however, that metamict zircon tends to be "more altered" than non-metamict zircon in zoned material. Also, irradiated diamond etches (in molten KNO_3) more rapidly after radiation damage [35] and the technique of fission track etching in minerals depends on the higher solubility of the damaged region [36, 37]. However, this "development" can only be brought about by very specific, corrosive etchants which selectively attack the damaged region. Fission tracks can also be developed in glasses [36], showing that these kinds of radiation effects in waste forms will not be confined to crystalline materials. In general, it would then be expected that radiation damage would be no more drastic in increasing the solubility or leachability than the typical change in solubility between the crystalline and glass form at the same composition. Further, if one considers isodesmic phases, such as zircon or monazite, where all the bond strengths are very high, the crystalline \rightarrow non-crystalline transformation should make relatively little difference to the solubility, since the weakest bonds are essentially unaffected.

5. Conclusions

On the basis of these arguments, one can draw the following conclusions.

(1) Non-crystalline phases exist in an infinite variety of structures. At present, only a crude genetic classification [8] helps to group certain such structures. Glasses ($\text{L} \rightarrow \text{S}'$) and metamict solids ($\text{S} \rightarrow \text{S}'$) although similar will, in general, have different structures, but the differences will not be able to be categorized in terms of the presence or absence of crystalline microphases.

Care needs to be exercised in describing members of the NCS family.

(2) As a first approximation, one can hypothesize that the changes of solubility properties of a crystalline phase when metamictized would be approximately equal to those incurred in transforming the crystal into a glass (of the same composition). In properly-designed solid radioactive waste forms, in which the actinides are constrained to be in radiation-resistant phases like uraninite or monazite (see also [38]), the effects of radiation damage on significant properties are likely to be quite small.

Acknowledgement

This research was performed under subcontract with Rockwell International under Contract DE-AC09-79ET41900 with the Department of Energy.

References

1. R. F. HAAKER and R. C. EWING, *Amer. Mineral.* **64** (1979) 1131.
2. R. M. BERMAN, *ibid.* **63** (1978) 807.
3. L. A. BURSILL and A. C. McLAREN, *Phys. Stat. Solidi* **13** (1966) 331.
4. E. R. VANCE, *Radiation Effects* **24** (1975) 1.
5. E. R. VANCE, L. EFSTATHIOU and F. H. HSU, *ibid.* **52** (1980) 61.
6. R. ROY, *J. Amer. Ceram. Soc.* **43** (1960) 670.
7. *Idem*, in "Symposium on Nucleation and Crystallization in Glasses and Melts", edited by M. Reeser, (American Ceramic Society, Columbus, Ohio, 1962) pp. 39-45.
8. *Idem*, *J. Non-cryst. Sol.* **3** (1970) 33.
9. *Idem*, in "Advances in Nucleation and Crystallization of Glasses", edited by L. L. Hench and S. W. Frieman, (American Ceramic Society, Columbus, Ohio, 1971) pp. 51-60.
10. J. H. KONNERT and J. KARLE, *Science* **179** (1972) 177.
11. R. ROY, *ibid.* **184** (1974) 91.
12. S. M. BRAWER and W. B. WHITE, *J. Chem. Phys.* **63** (1975) 2421.
13. T. MORIYA, *Bull. Tokyo Inst. Tech.* **66** (1965) 29.
14. W. PRIMAK, *Phys. Rev.* **110** (1958) 1240.
15. *Idem*, in "Ceramic and Glass Radioactive Waste Forms", edited by D. W. Readey and C. R. Cooley, Energy Research and Development Association Workshop publication number CONF-770102 (1977), pp. 157-176.
16. M. C. WITTELS and F. A. SHERRILL, *Phys. Rev.* **93** (1954) 1117.
17. D. T. KEATING, *Acta Cryst.* **16** (1963) A113.
18. R. M. BERMAN, M. L. BLEIBERG and W. YENISCAVISH, *J. Nucl. Mater.* **2** (1960) 129.
19. E. R. VANCE and J. N. BOLAND, *Radiation Effects* **26** (1975) 135.
20. P. H. GASKELL and D. W. JOHNSON, *J. Non-cryst. Sol.* **20** (1976) 153.
21. H. M. NAGUIB and R. KELLY, *Radiation Effects* **25** (1975) 1.
22. R. ROY and C. P. BUHSMER, *Amer. Mineral.* **50** (1965) 1473.
23. *Idem*, *J. Appl. Phys.* **36** (1965) 331.
24. D. S. BILLINGTON and J. H. CRAWFORD, Jr, "Radiation Damage in Solids", (Princeton University Press, Princeton, 1961) pp. 233-234.
25. F. A. MUMPTON and R. ROY, *Geochim. Cosmochim. Acta* **21** (1961) 217.
26. G. H. KINCHIN and R. S. PEASE, *Repts Prog. Phys.* **18** (1955) 1.
27. T. TAKAMORI and R. ROY, in "Advances in Nucleation and Crystallization of Glasses", edited by L. L. Hench and S. W. Frieman (American Ceramic Society, Columbus, Ohio, 1971) pp. 173-182.
28. G. MALOW and H. ANDRESEN, in "Scientific Basis for Nuclear Waste Management", edited by G. J. McCarthy (Plenum Press, New York, 1979) pp. 109-115.
29. L. S. HOBBS, *J. Amer. Ceram. Soc.* **62** (1979) 267.
30. M. R. PASCUCCI and L. W. HOBBS, *Bull. Amer. Ceram. Soc.* **59** (1980) 395.
31. L. A. BURSILL, E. A. LODGE and J. M. THOMAS, *Nature* **286** (1980) 111.
32. M. J. WEBER, R. P. TURCOTTE, G. R. BUNNELL, F. P. ROBERTS and J. H. WESTSIK, Jr, in "Ceramics in Nuclear Waste Management", DOE publication number CONF-790420 (1979) pp. 294-299.
33. G. J. MCCARTHY, W. B. WHITE and D. E. PFOERTSCH, *Mat. Res. Bull.* **13** (1978) 1239.
34. R. F. HAAKER and R. C. EWING, in "Ceramics in Nuclear Waste Management", DOE publication number CONF-790420 (1979) pp. 305-309.
35. M. J. MENDELSSOHN, Ph.D. thesis, University of London, (1971).
36. R. L. FLEISCHER and P. B. PRICE, *J. Appl. Phys.* **34** (1963) 2903.
37. *Idem*, *Science* **207** (1980) 979.
38. P. H. PERMAR and W. R. McDONELL, ASTM Proceedings of the 10th International Symposium on the Effects of Radiation in Materials, ASTM Committee E-10 on Nuclear Technology and Applications, Savannah, Georgia, June, 1980, to be published.

Received 2 September and accepted 22 September 1980.