Understanding resistance to amorphization by radiation damage

TOPICAL REVIEW

Understanding resistance to amorphization by radiation damage

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Abstract
Decades of experimental and theoretical studies have brought some useful insights about what defines resistance to amorphization by radiation damage; however, the problem is still viewed as generally unsolved. I review ideas and concepts that have been put forward to help with understanding this problem. I then discuss how the type of interatomic force is relevant for resistance to amorphization, with covalency of bonding stabilizing the damage and making material amorphizable. On a more detailed level, I suggest that resistance to amorphization of a complex non-metallic material is defined by the competition between the short-range covalent and long-range ionic forces. I follow this with a review of experimental data on 116 materials, to illustrate that the type of interatomic force can generally explain the resistance to amorphization. I conclude by discussing how the proposed picture is related to models proposed previously, and by suggesting some possible future research.

(Some figures in this article are in colour only in the electronic version)

Contents

1. Introduction

The wide interest in radiation damage processes has been stimulated by the number of important technological applications, including those in the nuclear power industry, the semiconductor doping industry, space applications and others. Since the strong influence of irradiation on the properties of surrounding materials was realized, the associated physical effects became a separate field of study attracting physicists, materials scientists and engineers. A brief search on the Web of Science search engine generates over 23 000 papers, published in the last 23 years, which have terms the 'radiation damage', 'ion implantation' or 'ion bombardment' in their titles or abstracts.

Irradiating a crystalline material with heavy energetic ions results, at least initially, in severe disruption of its order, leading to the appearance of a state termed radiation-induced 'amorphization' and material becoming 'x-ray amorphous'. Amorphization dramatically affects many properties of a material. Examples include altering mechanical durability of metals or other irradiated materials, increasing chemical transport in complex oxides, side effects related to the amorphization of a doped semiconductor. Novel materials, resistant to radiation damage, are constantly being searched for. This includes work as regards not only current processes, but also future applications such as in fission reactors [1].

Our interest in radiation damage effects comes from the problem of safe handling of radioactive materials that are of no use to us, but possess enough activity to pose a danger to the living environment. These include highly radioactive nuclear waste from nuclear power stations. Its safe encapsulation is often linked to the future of nuclear power, but even regardless of this, the currently accumulated amount of highly radioactive nuclear waste is sufficiently large to present us with the problem of its safe storage. An additional source of radioactive materials is surplus Pu. Some of it can be reprocessed into the mixed fuel oxide to be burned in nuclear reactors, but the high cost of this process and the risk of proliferation are often used to argue against reprocessing and in favour of encapsulation [2]. Vitrification, or immobilization of nuclear waste in glasses, has been a traditional method of encapsulation, but it has been recently recognized that crystalline oxide ceramics offer better durability and stability as encapsulation matrices (waste forms), and several ceramics have been proposed for encapsulating highly radioactive nuclear waste and surplus Pu [3–6]. A number of other materials are being actively investigated as possible waste forms, including TiO_2, perovskite $CaTiO_3$, zirconolite $CaZrTi_2O_7$, zirconia ZrO_2, zircon $ZrSiO_4$, pyrochlores $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$, APO_4 monazites and other complex ox- ides [7–52].

Under irradiation, a waste form may experience a large sharp percolation-type increase of chemical transport which reduces its ability to serve as an effective immobilization barrier. During alpha decay, a heavy recoiling atom inflicts the most structural damage, by creating several thousands of permanently displaced atoms [53]. As the radiation dose increases, the local damaged regions connect to form a percolating cluster, which provides a macroscopic pathway for increased transport of chemical species. These include radioactive isotopes which

may diffuse out in the environment [57, 58]. Because some radioactive isotopes are long lived, a waste form should remain an effective immobilization barrier on the timescale of up to a million years. In this context, the search for materials that are resistant to amorphization by radiation damage is currently under way.

Apart from the waste forms, understanding of resistance to amorphization is important for a wider community as well. For example, this includes the large semiconductor doping industry, and there has been active research into semiconductors with increased resistance to amorphization by radiation damage (see, for example, [54–56]).

Experimental results on resistance to radiation damage are strikingly diverse. Some materials amorphize readily under irradiation by heavy ions, while others do not show any loss of crystallinity even at extremely high radiation doses and cryogenic temperatures. Once this had been realized, the question of the physical origin of resistance arose, and remains open. Why are MgO and Al_2O_3 much more resistant to amorphization than any form of SiO_2 or GeO_2? Why is ZrO_2 more resistant to amorphization than TiO_2? Why are all complex silicate and titanate oxides, regardless of their structure and chemistry, readily amorphized? Why are complex silicate oxides more prone to amorphization than structurally similar phosphates? What makes $Gd_2Zr_2O_7$ pyrochlore, yet another 'champion' in resistance to amorphization, greatly superior to $Gd_2Ti_2O_7$, a structurally similar pyrochlore that amorphizes readily? Why does the resistance of $Gd_2Zr_xTi_{2-x}O_7$ consistently increase with x? What makes $La_2Zr_2O_7$ pyrochlore more resistant than structurally identical $La_2Hf_2O_7$ pyrochlore, which, in turn, is considerably more resistant than $La_2Sn_2O_7$ pyrochlore? Why is $Er_2Zr_2O_7$ greatly more resistant than $Er_2Ti_2O_7$? What is it about spinel $MgAl_2O_4$ that makes it much more resistant to amorphization than any complex silicate and titanate oxide such as Al_2SiO_5, Mg_2SiO_4, $FeTiO_3$, $MgTiO_3$? Why is Si_3N_4 very resistant to amorphization while SiC is readily amorphized? Why is GaN considerably more resistant to amorphization than GaAs? Why is ZnO resistant to amorphization while Si and Ge are amorphized readily?

The list of similar questions can be continued. More importantly, this list is growing as new experimental data are being accumulated.

Apart from technological stimuli, there should be exciting science behind radiation damage effects. Indeed, the most fundamental question in the area remains open, which is *why is there radiation damage in the first place*? What defines the stability to the structural damage induced by radiation and therefore resistance to amorphization? The common viewpoint is that the problem is complex and that the phenomenon is necessarily a combination of several, equally important and often competing effects. While appreciating the point about complexity, I will try to suggest that to a sufficiently large extent, understanding and predicting the resistance to amorphization can come from a single general physical parameter. I will also discuss factors which in the past contributed to the difficulty of understanding the resistance to amorphization and increased the seeming complexity of the problem, sometimes more than was justified by the relevant physics.

Several theoretical models of resistance to amorphization exist, and many more correlations of resistance with other materials properties have been proposed. These will be reviewed, without trying to be exhaustive, but rather to illustrate the range of directions undertaken in the area. I shall then attempt to propose that from the general physics of radiation damage, the resistance of a material to amorphization is defined by the competition between the long-range and short-range forces, originating from ionic and covalent contributions to bonding (in this work I consider non-metallic compounds, mostly with mixed covalent and ionic bonding). This is followed by a review of experimental results on 116 materials, to illustrate the point. I will conclude by discussing possible directions and challenges for further theoretical, experimental and computational studies of the problem.

2. Models of resistance to amorphization and associated parameters

In this section, I will discuss some of the concepts and mechanisms that have been invoked to gain insights into what controls the resistance to amorphization. A full comprehensive review is beyond the scope of this work and apologies should be tendered for possibly not mentioning some worthy works of which I am unaware. Rather, my aim here is to give the reader a feel for the range of ideas discussed.

2.1. Models related to structure, glass-forming ability and other properties

A significant proportion of models have related the resistance of a material to its geometrical structure, although they have done so in different ways and using different arguments. For example, it has been argued that the reason that $Er_2Zr_2O_7$ is dramatically more resistant to amorphization than $Er_2Ti_2O_7$ is because the ratio of cation radii in the former is smaller than in the latter, which reduces the energy cost for cation disordering. The ease with which cation disorder can be accommodated in the former makes it tolerant to structural changes induced by irradiation, and it has been suggested that this effect should take place in fluorite structures such as $Er_2Zr_2O_7$, whereas pyrochlore structures such as $Er_2Ti_2O_7$ should be more susceptible to amorphization [7, 8]. Arguments based on the relation of material structure to that of fluorite and the energetics of cation disorder, related to the relative sizes of ionic radii in a compound, have been used to gain insights into the high resistance of other ternary and binary oxides [9, 10, 20, 45]. Using related ideas concerning the ease of accommodating cation disorder, interesting predictions have been made recently regarding the resistance to amorphization of several ABO_3 compounds [46].

In a different study, comparing the resistances of ternary $ZrSiO_4$, Fe_2SiO_4, Mg_2GeO_4, $MgAl_2O_4$ and more complex oxides, it has been concluded that the structure type plays an important role in defining the resistance to amorphization, through the average O–O distance, the bond compression coefficients, the ratio between the M–O distances in tetrahedral and octahedral sites, the deviation of the O packing from perfect ccp and hcp packing and other parameters that depend on the structure [42]. Finally, in order to explain the smaller resistance of stannate pyrochlore relative to mixed zirconate and titanate, as well as other pyrochlores, it has been proposed that the former has a smaller degree of distortion of the SnO_6 polyhedron, due to the increased covalency of the Sn–O bond, which makes its structure deviate from the more resistant fluorite structure which can accommodate disorder more easily [44, 45].

For a wider range of materials, the 'topological' model has related radiation resistance to the topological freedom of a crystalline material [30–32]. With nearest bonds defining the number of local constraints of an atom, an underconstrained material has more structural freedom for alternative rearrangements than an overconstrained one, and hence it is more prone to radiation damage (it is implied that one of these alternative rearrangements could be the damaged state, which can be as 'acceptable' and stable as any other alternative crystalline arrangement).

In other works, the resistance to amorphization has been related to certain physical properties of a material. For example, in silicates, resistance has been found to correlate with target density, melting point, polymerization index, ionicity and elastic moduli [16, 42]. For titanate pyrochlores, the difference in resistance has been attributed to the different masses of target materials, because larger mass means larger cross-section and hence larger number of displaced atoms [19]. For ternary monazite and zircon structures, the ratio of electronic to nuclear stopping powers of a target material [14, 15] has been suggested to play a role in the resistance to amorphization (electronic stopping power is the energy loss due to the electronic excitation processes, whereas nuclear energy loss is due to 'ballistic' collisions

between nuclei): the higher the ratio, the higher the mobility of point defects, leading to a smaller number of defects. In a different study, the strength of the P–O bond was suggested to be related to the higher resistance of phosphate monazites relative to silicates with the related zircon structure [21]. Finally, the energy of the bond was mentioned as being an important factor in the resistance to amorphization of several nitrides and oxides [59, 60], with resistance increasing with the bond energy.

Resistance to amorphization has also been compared to the ability to form glass by liquid quenching. The idea that the easier the glass formation, the smaller the resistance to amorphization has given rise to several models. On the basis of the experimental results for several binary and ternary oxides and models of viscous melts, it has been suggested that the resistance to amorphization can be predicted from the glass-forming ability, quantified by a parameter that depends on the structure, the bond strength and the temperature of the transition between a solid and a liquid [11–13]. Using similar ideas, resistance to amorphization has been related to the efficiency of 'cascade quenching' in several pyrochlore structures [61] and to the ease of glass formation in several zirconolite structures [13].

In comparing resistance between ternary titanate oxides and alumina oxide, it has been noted that the resistance to amorphization increases with the melting point [17]. Finally, other experimental results also showed that the resistance of several tens of complex silicate oxides correlates with their melting points [16]. At this point the important early 1975 work of Naguib and Kelly should be mentioned. They discussed several criteria for resistance to amorphization by radiation damage, based on the available experimental data on the resistance of binary compounds [86]. Their first criterion for resistance was the temperature ratio criterion, based on the analogy between radiation damage and crystallization of liquid, and it implied that a material's resistance increases with increase of the melting temperature and decrease of the crystallization temperature. The second criterion was based on the good correlation of resistance with ionicity. The authors observed that materials with Pauling empirical ionicity lower than 0.47 are amorphized by irradiation, whereas those having ionicity higher than 0.59 are not. Several possible explanations of this correlation were mentioned. First, they suggested that radiation-induced amorphization is related to substitutional disorder whose energy cost is high in ionic materials due to large increase of electrostatic energy. Second, different bonding types result in different lattice strains caused by irradiation-induced defects. Finally, the directed nature and short-range character of covalent bonds were mentioned, although their implications for resistance to amorphization were not discussed. The overall conclusion was that the underlying physical model was not clear, and the type of bond criterion was considered to be of empirical origin.

2.2. Molecular dynamics simulations

I conclude this section with a discussion of molecular dynamics (MD) simulations of radiation damage. This technique has become popular in studying radiation damage effects. Extensive reviews have been written on this subject, describing the method [62, 63, 67]. Briefly, one simulates the propagation of an energetic particle in a system of atoms interacting via a model potential, by integrating the Newton equations of motion. This energetic particle displaces atoms from their equilibrium positions, which, in turn, displace other atoms, resulting in a 'radiation cascade'. At each moment of time, the simulation provides coordinates and velocities of all atoms in the structure, giving the full phase trajectory of damage propagation. At the end of the simulation, the resulting structure contains structural changes due to radiation damage, which can be analysed in detail. Shown in figure 1 is an example of the MD simulation of radiation damage produced by the close overlap of 50 keV recoils in zircon structure. Details can be found in [58].
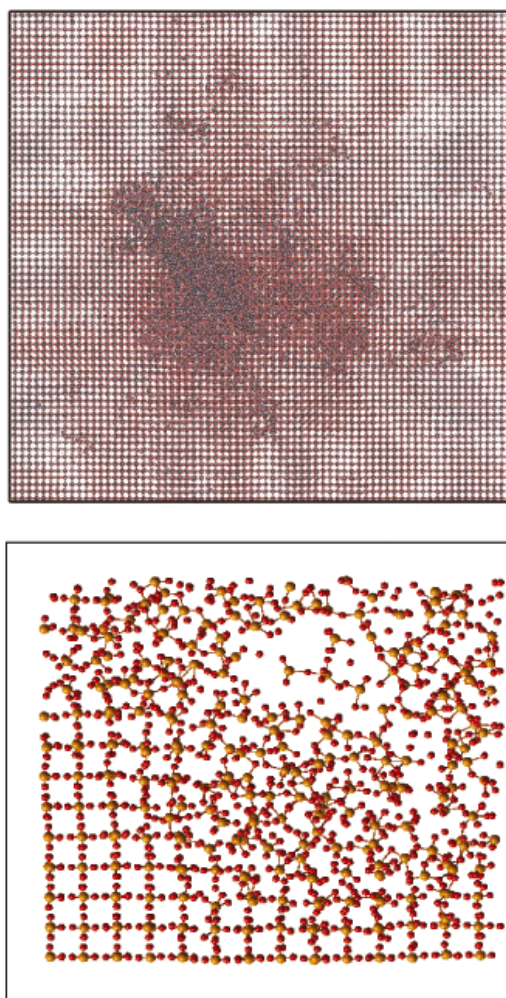
Figure 1. Top: zircon structure, damaged by closely overlapping 50 keV events. Bottom: a thin slice of the core of the damaged region showing connected disordered 'polymerized' Si–O chains. From [58].

Several limitations exist in MD simulations, including the limited system size and time, although some of these are being lifted. For example, the electrostatic interactions, required to simulate effective charges in many materials, are the major problem as regards the speed of simulation. However, with increasing computer abilities and improving efficiency of simulation codes, it is now possible to simulate systems with several million atoms whose interactions include electrostatics [66]. These simulations can be performed on parallel machines using up to several thousands of processors, each simulating a particular task. Fast communication between the processors is essential to increase the speed of simulation, as well as the MD parallelization strategy. One example is provided by the recent development of the DL_POLY MD code, a domain decomposition strategy [64, 66], in which each processor simulates a particular cluster of atoms in the system. With these and other similar developments, the issue of system size seems to have been overcome, in that the damage from recoils with realistic energies of typically 100 keV, and possibly more, can now be contained in the MD

simulation box. One of the existing drawbacks of MD simulations is that the simulation time is still limited to typically a few hundred picoseconds for large systems; however, important insights have still been obtained using this method.

MD simulations have given us the useful ability to visualize the radiation damage on the atomistic level and timescale. They have also been used to study resistance to amorphization in several materials. For example, an interesting MD study has addressed the large difference in resistance between titanate and zirconate pyrochlores. Energetic recoils with energy up to 20 keV were simulated in both materials [65]. The size of the radiation cascade in zirconate pyrochlore was found to be smaller than that for titanate pyrochlore, suggesting that the former is more resistant to radiation damage, consistent with experimental results [29] and studies based on the energetics of cation disorder discussed above [10].

In a different MD study, the difference in resistance to amorphization between elemental metals Al and Cu and semiconductors Si and Ge has been attributed to the difference in structure: more open tetrahedral structure in semiconductors allows the fast atoms to travel larger distances and create more damage, whereas atomic collisions in metals are confined to smaller regions because metals are close packed, resulting in smaller damage size [67, 68]. In another set of MD simulations, the difference in resistance of GaN relative to Si, Ge and GaAs has been attributed to the different threshold displacement energy, the energy needed to displace an atom from its equilibrium position in crystalline structure. This energy is higher for GaN than, for example, for GaAs (which has been related to a greater hardness of the former) and therefore GaN is more resistant simply because the threshold displacement energy is larger and therefore the initial damage is smaller [69].

Finally, on the basis of MD results, it has been suggested that in silicates such as zircon $ZrSiO_4$, the damaged structure is stabilized by the formation of disordered polymerized Si–O network [70–72] (see figure 1). The empirical potential, although fitted to the equilibrium structure, reproduced the formation of a disordered network, consistent with the known tendency of polymerization of covalent silica networks. The formation of a polymerized Si–O network in damaged zircon structure has also been confirmed by experimental NMR studies [53] and quantum-mechanical calculations [73]. In a recent study, classical MD simulation was used to simulate radiation damage in perovskite, $CaTiO_3$ [87]. Quantum-mechanical calculations were then employed to relax the elements of the damaged structure. These calculations showed that amorphization in perovskite is due to the formation of disordered Ti–O chains with appreciable covalency in bonding.

2.3. Discussion

The ideas and insights discussed above have been useful for our understanding of the problem, because they touched upon several possibly important aspects of the physics behind the resistance to amorphization. I have mentioned about 20 factors that have been named as relevant to the problem. A more comprehensive review can probably increase this number, but it seems already large enough to ask whether the problem is indeed a combination of several important mechanisms, each working differently in every class of materials and for every set of experiments or simulations, or whether there might exist a single most relevant mechanism. Finding this mechanism is a tantalizing task for a physicist, and is based on the belief that one should always try to look for generality in phenomena, by singling out the most relevant process(es) in them. This does not mean that if such a general mechanism exists for resistance to amorphization, others are irrelevant; however, they should not be the manifestation of the same mechanism, i.e. they should not be dependent variables.

The views of researchers as regards how well we understand the resistance to amorphization vary, but the common viewpoint is that the problem cannot be considered

as generally resolved. This is best seen when one tries to *predict* the resistance of a material on the basis of any of the previously proposed criteria. For example, it has been pointed out that a particular geometrical structure of a material may not uniquely define high resistance to amorphization, because materials with other structures also show remarkable resistance [47]. Next, a more general topological criterion, that relates high resistance to amorphization to overconstrained structures, does not predict the remarkably different resistances of materials that are topologically identical or similar (see the discussion in section 4). Similarly, a glass-forming criterion does not predict the resistance of materials that do not form glasses by conventional liquid quenching, but are nevertheless readily amorphized by radiation damage, with Si and Ge providing obvious examples (see section 5 for more detailed discussion). Finally, the relation between the resistance and other physical properties such as hardness, elasticity, density and other parameters may not be used to predict resistance either: materials with similar resistances may have very different values of these parameters. At the same time, materials with close values of these parameters may show very different resistance to amorphization (see section 4).

The challenge of predicting resistance to amorphization also remains for MD simulators. To a large extent, the outcome of the MD simulation of radiation damage is defined by how well the interatomic potential describes interactions far from equilibrium. This is a problem, since often the empirical potential is fitted to structures at equilibrium. Still, even if good potentials existed for many materials and would reproduce the experimental behaviour of the resistance, the question still remains of what is it about a given potential that results in high or low resistance. Next, because the potential is related to the geometrical structure, MD simulation does not decouple the effects of the potential from the effects of the structure; hence one is left wondering how structure may affect the resistance in a given simulation. Finally, both the structure and the potential govern other physical properties such as the bond energy, elasticity, hardness, ionicity, and these parameters may be thought to affect resistance as well. In brief, the MD simulation does not give an unambiguous answer to the problem.

In the next section I will discuss how the type of interatomic force is relevant for resistance to amorphization, and propose that resistance is governed by the competition between the long-range ionic and short-range covalent forces.

3. Resistance to amorphization by radiation damage and interatomic forces

3.1. Relevance of the bonding type

The experiments point to the resistance being defined by the structure's ability to regain the initial crystalline state following the damage. This includes the systematic increase of the radiation dose, after which the structure becomes 'x-ray amorphous', with increasing temperature, signalling that 'recrystallization' is a thermally activated process. If the structure of a condensed phase is entirely defined by the interactions between constituent particles, what type of interaction would stabilize the damage produced by irradiation and make a material amorphizable?

The interatomic interactions are electromagnetic in origin, and depend on the distribution of electronic charge density. One is immediately led to consider how this distribution is varied in different materials. This distribution is commonly related to the type of the chemical bond [74], and in this section I will discuss how covalency and ionicity may give rise to different behaviours of resistance to amorphization.

It should be noted at this point that discussion of the concepts of 'ionicity' and 'covalency' often meets an objection that they are not clearly defined, particularly that a bond often has considerable contributions from both types, and that drawing a line between the two cases

is not straightforward. Indeed, if a solid is called 'ionic', this often only means that some properties can be described using an ionic model, and one has to be careful not to overstretch model-related concepts such as ionic radius into the cases where the model is inadequate [75]. However, the two polar cases of ionic and covalent bonding can still be well defined using the numbers derived from the distribution of electronic density between atomic cores [74]. If these concepts are used in this sense only, then the challenge lies not in the definitions, but in the fact that no unique prescription exists for quantifying these concepts [76]. However, this does not mean that no distinction can be made between materials which are *qualitatively* different in their types of interatomic interaction, on the basis of the electronic density between atomic cores. In covalent and ionic extremes, this density can be different by up to two orders of magnitude [74]. I will try to suggest that such a difference may result in dramatic differences in resistance to amorphization by radiation damage, because it influences the ease of atomic rearrangements.

As mentioned above, bond ionicity was proposed, among other empirical criteria, as a relevant factor for resistance to amorphization, by Naguib and Kelly in 1975 [86]. Since they concluded that the physical model, relating bond ionicity to resistance, was not clear, this criterion has remained empirical. Since this work was published, bond type has been fragmentarily mentioned in the literature as one of the possible relevant issues in radiation damage, while other models and theories have been proposed and developed. It can be speculated that there were several reasons for this, including the fact that the physical model was not clear. Next, whereas ionicity can be defined for a binary compound (using Pauling, Phillips or other definitions), no accepted recipe exists for a complex compound. Finally, even for a binary compound, the value of empirical ionicity may not reflect the distribution of electronic density correctly. This is especially true for oxides, as is seen by comparing their empirical ionicities with the electronic density maps, obtained by either experiments or quantum-mechanical calculations (see the detailed discussion in section 4). As a result, it is often concluded that ionicity (as calculated from the electronegativity values) shows no correlation with experimental values of resistance (see, for example, [77, 45]). I suggest that this has particularly contributed to the belief that bond type may not be relevant for resistance to amorphization and stimulated the development of other models and approaches. As I will discuss in this work, resistance to amorphization shows, in fact, a very good correlation with the type of bonding, provided that this type is judged on the basis of electronic density maps obtained either experimentally or from quantum-mechanical calculations.

It needs to be stressed at this point that a reliable conclusion about the type of bonding can only be reached if one returns to the definition of the terms covalency and ionicity, and analyses the electronic density maps. These have become available relatively recently, with the advance of experimental methods and quantum-mechanical calculations. Other factors have also contributed to the possibility of the present discussion, including the increasing experimental database. The number of experimental data available has grown enormously in the past few decades, allowing better systematization and a more focused discussion. Finally, our understanding of how long- and short-range forces can be relevant for the formation of ordered patterns and hence for the resistance to amorphization has been recently advanced, allowing for a more solidly based theoretical discussion.

The simplest microscopic picture of resistance to radiation damage can be briefly discussed as follows. The energy of a recoiling atom in alpha decay is of the order of 100 keV, and laboratory experiments use heavy ions with energies of several megaelectronvolts. A heavy energetic ion with an energy in this range knocks out all the atoms along its path which, in turn, displace other atoms, leading to the creation of a highly disordered damaged region, a radiation cascade. In zircon, for example, a recoiling atom from an alpha decay causes several thousands

of permanent displacements of atoms, which form a radiation cascade a few nanometres in size (see figure 1). At higher energies, an energetic ion also loses its energy by electronic excitations. Part of the initial recoil energy is transformed into the potential energy of the damage, while the remaining part is dissipated into the matrix as thermal vibrations. A useful insight from earlier computer simulations of radiation damage is that, as the energy is dissipated into the matrix, there is a considerable atomic mixing in the cascade, equivalent to local 'melting' [81–84]. The radiation cascade, at least in some materials, can be approximately thought of as a highly disordered mixed 'soup' of the constituent elements of the material. At the initial stages of damage evolution, the cascade morphology does not depend on the nature of the interatomic forces at equilibrium. This is because, at high energies, the interatomic interactions are defined by the strong short-range repulsion forces only. As the energy dissipates into the matrix, the interactions between atoms in the damaged region become comparable with their kinetic energies. It is at this point that the nature of interatomic forces at equilibrium comes into play and defines what arrangement atoms adopt in post-irradiated structure, thus crucially influencing what we call the resistance to amorphization by radiation damage of a material.

If the structure of a condensed phase is entirely defined by the interactions between constituent particles, what type of interaction would stabilize the damage produced by irradiation and make a material amorphizable?

Before discussing this point in detail, I note that some insights into this question can be gained from the MD simulations of radiation damage in complex silicates and titanates [71, 72, 70, 87]. It has been observed that the damaged structure contains disordered Si–O–Si and Ti–O–Ti bridges, whose stability in the damaged state prevents atoms from regaining coherence with the crystalline lattice. Figure 1 shows a slice of the damaged structure of zircon, in which only Si and O atoms are shown. Once formed in the radiation cascade, disordered Si–O chains remain stable, preventing any 'recrystallization'. Note that there is a substantial covalent contribution to the Si–O bonding which promotes network forming. In MD simulation, the tendency to form networks is simply emulated by the functions in the interatomic potential. One can generalize this result and state that *a material is amorphizable by radiation damage if its chemistry allows it to form a covalent network*. This is discussed below in detail.

In simple terms, the relevance of the type of interatomic force for resistance to amorphization can be discussed as follows. After the displacement of atoms by propagating heavy ions, the rearrangement of atoms needed to regain coherence with the crystalline lattice involves significant atomic motion. In a covalent structure, the interactions can be thought of as short-range directional constraints, due to the substantial electronic charge being localized between the neighbouring atoms. Therefore cooperative atomic motion is 'hooked' by the electrons between neighbouring atoms, and requires breaking directional covalent bonds with the associated energy cost [88]. On the other hand, highly ionic structure can be viewed as a collection of charged ions. The cooperative rolling of spheres which are only electrostatically charged does not require additional activation energy [88], giving damaged ionic structure better chances to re-establish coherence with the crystalline lattice. The same mechanism is behind the fact that the melt viscosity is higher in a covalent structure than in an ionic one, which has consequences for glass-forming ability [88]. An example from yet another area is that higher ionicity results in higher ionic conductivity, since higher ion mobility increases transport of carriers [89, 90].

Moreover, in a material with high ionicity of bonding, the local recrystallization process is promoted by the need to compensate electrostatic charges, with an ion attracting oppositely charged neighbours and making the 'defect' structures that consist of neighbouring atoms of the same charge energetically unfavourable. This effect is absent in a covalent structure.

Finally, additional insight concerning the relevance of the type of interatomic force for the resistance to amorphization comes from the consideration of the energy landscape created by long-range (ionic) and short-range (covalent) forces. The latter result in landscapes with many closely related minima, whereas the former lead to landscapes with significantly fewer minima [91]. Hence the damaged structure can stabilize in one of the many alternative minima in a material with dominating short-range covalent forces, whereas it is much more likely to decay towards a crystalline minimum in a structure with dominating long-range electrostatic forces.

If 'recrystallization' (re-establishing coherence with the crystalline lattice) is permitted by the interatomic forces, the crystalline lattice around the radiation cascade provides a template for such recrystallization. Atoms near the interface between the crystalline lattice and radiation cascade lose their kinetic energy through dissipation faster than those in the core, and settle on the crystalline positions provided by the crystalline template. In this picture, 'recrystallization' can be viewed as growth of the interface inside the radiation cascade.

In this discussion it is assumed that electronic relaxation takes place much faster than relaxation of atoms, and that electronic defects play a minor role in local recrystallization processes. It should be noted that electronic defects (related to changes in the electronic structure due to excitation, ionization and other processes) become pronounced at large, megaelectronvolt energies, and play a role in stabilizing the damage, as will be discussed in section 6. The reader is referred to the detailed discussion of electronic defects in radiation damage [78–80].

3.2. Resistance to amorphization of a complex compound

The picture of resistance discussed above gives insights into the resistance to amorphization of a binary compound with partial ionic/covalent bonding. However, a radiation cascade, created in a complex material, can contain several distinct chemical phases with different degrees of ionicity/covalency between different atomic pairs. For example, most of the currently considered waste forms are ternary oxides. How can one describe the resistance to amorphization in this complex case?

Assuming that for a given atomic pair, the contribution of long-range forces to the force field (or Hamiltonian) can be approximately defined by the values of effective charges, with the rest coming from the short-range interactions, one can get the contributions of long-range and short-range forces. Then the total force field in a complex compound can be approximated, at least in principle, as the sum of short-range and long-range forces, each part being a sum of respective contributions to the short-range and long-range forces within a pair. Now, the resistance to amorphization of a complex compound can be formulated using the arguments discussed above, by stating that short-range covalent and long-range ionic forces compete in creating a potential energy landscape with a certain number of minima and distribution of activation energy barriers. What is meant here by competition? First, as discussed above, short-range covalent forces increase energy barriers to local rearrangement processes (through the 'hooking' mechanism, as discussed above), while barriers in the system with long-range ionic forces are smaller. Changing the contributions of both components is expected to modify the energy landscape accordingly. Next, the need to compensate opposite charges in a system with a long-range ionic contribution to the force field promotes activation over the energy barriers and reduces the likelihood of 'defect' structures, composed of the same charges. This effect increases as the weight of the long-range component in the force field increases. Finally, short-range and long-range forces compete in increasing and reducing the number of potential energy minima, respectively. Hence one can generally state that the efficiency of

damage recovery and hence *resistance to amorphization of a complex material is defined by the competition between the long-range and short-range forces*, originating from the ionic and covalent contributions to bonding, respectively.

It is interesting to note that the winning of such a competition by long-range forces leads to the appearance of ordered formations in electronic systems [92, 93].

The advantage of the definition, based on the competition between long-range (ionic) and short-range (covalent) forces, is that it can be applied to a material of any complexity. For example, the resistance of an ABO oxide can be generally predicted from the type of A–O and B–O bonding. If SiO_2 is readily amorphizable, one would expect any complex silicate to be generally susceptible to amorphization, since the short-range covalent forces would be expected to dominate and stabilize the disordered silica phase and the overall damage.

4. Experimental results on resistance to amorphization

4.1. Discussion

In this section I illustrate the theoretical discussion of resistance, offered in the previous section, with experimental examples. Experimentally, the resistance can be measured by the critical amorphization dose, D_c, the radiation dose after which a material becomes 'x-ray amorphous'. The higher D_c, the more resistant the material. Another measure of resistance which is often used is the critical amorphization temperature, the temperature after which a material cannot be amorphized by irradiation, T_c. The higher T_c, the lower the resistance.

The experimental data on resistance discussed below have been obtained by various groups using different experimental conditions. Changing these conditions, such as the ion mass and energy, can significantly alter the measure of resistance, as will be discussed below in more detail. Whenever a material below is called 'resistant', it often means that D_c is unusually high (or T_c is unusually low) relative to those of other materials irradiated under the same conditions. Some of the highly resistant materials discussed below cannot be rendered amorphous at any radiation dose. On the other hand, silicates, for example, are often used as a benchmark for materials with low resistance. The materials below are grouped into classes defined mostly by their chemistry and resistance to amorphization in a sense discussed above.

• SiO_2 is amorphized relatively easily [16], as expected in the proposed picture, due to the substantial covalent contribution to the Si–O bond. The above-mentioned transferability of the proposed criterion means that any silicate should amorphize relatively easily, since the covalent silica network stabilizes the damaged structure. This is indeed what is observed [11, 12, 14, 16, 22, 57]. The above references include over 40 different complex silicate structures, with various chemistries, structures, topologies, melting points, glass-forming abilities and other properties and parameters, that are readily amorphized by ion irradiation.

• Similarly, two polymorphs of GeO_2 are found to be readily amorphizable by radiation damage [38], due to the substantial covalent contribution to the bonding, as are complex germanites such as Mg_2GeO_4 [42].

• TiO_2 is relatively sensitive to radiation-induced amorphization, as compared to the highly resistant compounds discussed below [5, 9, 95]. At this point it should be stressed again how the covalency or ionicity of a compound can be reliably judged. Electronegativity tables [97] can be used as general guides for quantifying the bond ionicity; however, it is often not possible to reliably compare the ionicity of two compounds with close values of electronegativity difference (see, for example, [98] and the discussion below). The only reliable way to determine the bonding character is to analyse the electronic density maps, obtained from either experimental diffraction methods or quantum-mechanical calculations.

Perhaps it may come as a surprise (in a sense that it is 'against the chemical intuition' [105]), that there is a considerable covalent contribution to the bonding in TiO_2. The evidence for this comes from both diffraction methods and quantum-mechanical calculations [87, 99–102]. Note that TiO_2 is more resistant than SiO_2 and GeO_2 [38], presumably due to the larger ionicity in the bonding than in the classical network formers SiO_2 and GeO_2.

Just like complex silicates, complex titanates are readily amorphizable by radiation damage: for example, the perovskites $CaTiO_3$, $SrTiO_3$, $BaTiO_3$, pyrochlores $Gd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Eu_2Ti_2O_7$, $Y_2Ti_2O_7$, zirconolite $CaZrTi_2O_7$, ilmenite $FeTiO_3$, geikelite $MgTiO_3$, hollandite $BaAl_2Ti_5O_{14}$ and other compounds are amorphized relatively easily [7, 8, 13, 15, 17, 19, 28, 29, 48, 116, 51]. According to the proposed criterion, the titania phase that consists of disordered covalent Ti–O–Ti bridges stabilizes the damage in complex titanates, making them amorphizable.

To illustrate this discussion, figure 2 shows electronic density maps calculated for damaged $CaTiO_3$ perovskite structure, containing disordered covalent Ti–O–Ti bridges. The electronic structures of ideal perovskite structure and rutile TiO_2 are also shown.

• As discussed above, the barriers to regaining coherence with the crystalline lattice are reduced in compounds with high ionicity in bonding, making them significantly more resistant to amorphization.

The binary oxides MgO, ZrO_2 and Al_2O_3 are known to be highly resistant to amorphization by radiation damage as compared to readily amorphizable silicates and titanates [11, 12, 17, 18, 9, 23, 24, 32, 94, 96]. MgO and ZrO_2 show no loss of crystallinity under ion bombardment even at high radiation doses. High resistance of ZrO_2 has also been confirmed by means of Pu doping [40, 41]. The evidence for high ionicity of these binary oxides comes from the electronic density maps derived by both experimental and computational methods. High ionicity of bonding has been concluded for Al_2O_3 [103–108], MgO [98, 107, 108] and ZrO_2 [87, 109, 110]. The electronic density maps calculated for damaged MgO and ZrO_2 are also shown in figure 2.

Similar to the case of TiO_2, this example shows that in order to correctly predict resistance, the analysis of electronic density maps is required. The result of such analysis may, perhaps, appear 'against chemical intuition' [105]: indeed, applying the empirical ionicity criterion using Pauling electronegativities to Al_2O_3 would give it an ionicity value very similar to that of TiO_2. Thus this approach would predict similar resistances of the two compounds, whereas Al_2O_3 is more resistant than TiO_2, in good agreement with the character of bonding as revealed by the electronic density maps.

• If the binary AO and BO oxides are highly ionic (e.g. MgO and Al_2O_3), it is likely that the ionicity of a ternary oxide ABO is not altered significantly relative to the binaries, and hence an ionic ternary is expected to be resistant to amorphization. The electronic density maps of spinel, $MgAl_2O_4$, show a high degree of ionicity [107]. At the same time, this spinel is known to be highly resistant to amorphization radiation damage [25, 28, 96]. The same line of argument can be used to explain the extreme resistance of zirconate oxides $Gd_2Zr_2O_7$, $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Ce_2Zr_2O_7$ and $Er_2Zr_2O_7$ [7, 8, 20, 29, 52]. To the best of my knowledge, no detailed information exists on the electronic density maps of these zirconate pyrochlores. However, as discussed above, bonding in ZrO_2 shows significant ionic character, and our preliminary results show that the ionicity of Zr–O bond is not altered significantly when Zr changes its eightfold O coordination in ZrO_2 to the sixfold coordination in the ternary zirconate oxides above [112]. Hence one can speculate that the bonding in these ternary zirconate oxides is highly ionic in character. Note that $La_2Zr_2O_7$ is the only known zirconate oxide that can be amorphized, due to the large value of the ratio of cation radii [20]; however, it is still considerably more resistant than silicate and most titanate oxides.
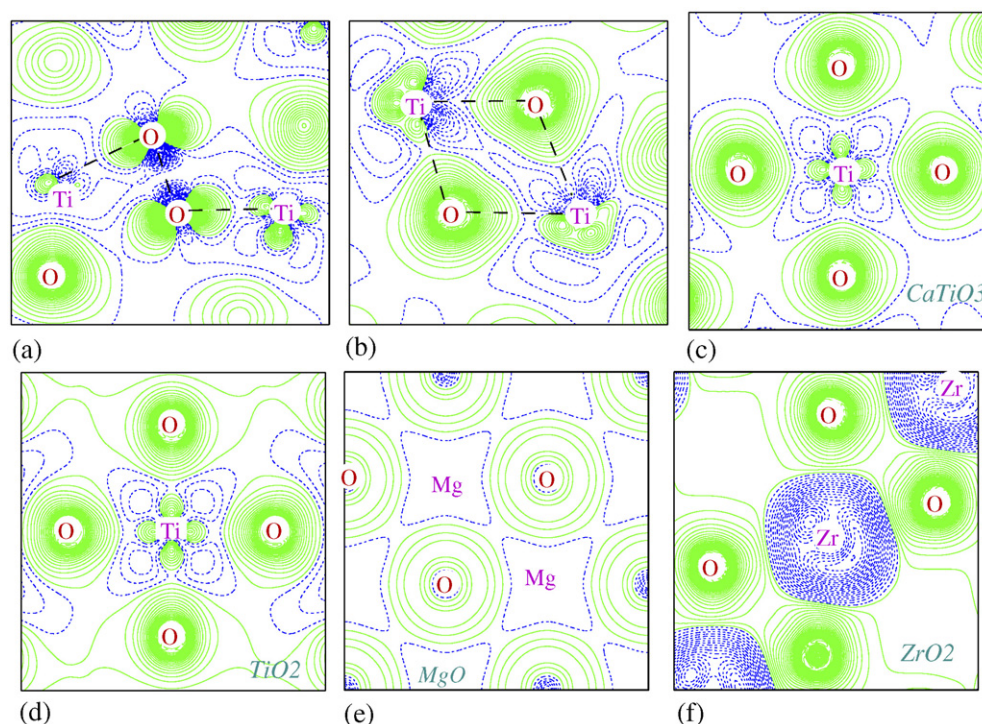
Figure 2. Contour plots of the electronic deformation density, $\delta\rho$, calculated for ((a), (b)) two relaxed defects in damaged CaTiO$_3$ structure, (c) crystalline CaTiO$_3$, (d) crystalline rutile TiO$_2$, (e) crystalline MgO, and (f) crystalline ZrO$_2$. In crystalline structures, the contour plots are drawn for the cation–anion plane, and in defected structures the plane was defined by the two O and Ti atoms. The contour plots are drawn between $-0.25e$ and $0.25e$, and each line corresponds to a step of $0.006e$. Blue and green lines correspond to negative and positive values, respectively (dashed and solid lines in the black and white version of the figure). In defected perovskite ((a), (b)), Ti–O bonding is directional, as seen by the deformation of the electronic charge between neighbouring Ti and O atoms. This covalency of the Ti–O bonding can also be seen in the crystalline perovskite and rutile ((c), (d)). In defect 1 (a), the directionality in $\delta\rho$ can also be seen along the O–O line. In defect 2 (b), there is no deformation of $\delta\rho$ between two O atoms, and the edge-shared defect is formed by each Ti atom forming a covalent bond with two O atoms. In all cases, the analysis of the overlap Mulliken population shows appreciable charge between Ti–O atoms forming a covalent bond. In contrast to the covalent character of the bonding in (a)–(d), no directionality is seen in $\delta\rho$ for the highly ionic MgO and ZrO$_2$. From [87].

The examples above demonstrate how the ability to form a covalent network makes a material amorphizable by radiation damage. The importance of chemical control can be demonstrated particularly well by comparing materials which contain, or do not contain, elements that can form a covalent network. Examples are given below.

• The remarkable difference in resistance to amorphization between two spinels MgAl$_2$O$_4$ and SiFe$_2$O$_4$ has been noted, with the former spinel being remarkably resistant and the latter one being readily amorphizable [39]. The difference between the two spinels is readily explained in the proposed picture: MgAl$_2$O$_4$ shows a high degree of ionicity in bonding, whereas SiFeO$_4$ can form a disordered covalent network due to the substantial covalency in the Si–O bond. The remarkable resistance of spinel, MgAl$_2$O$_4$ [25, 28], has also been contrasted with the ease of amorphization in all three polymorphs of Al$_2$SiO$_5$ [11, 12]. In the proposed picture, the difference between the two compounds comes from Si substituting for the Mg atom and

introducing covalency in the bonding. Next, the replacement of Al by Si in spinel also results in a dramatic decrease in resistance: the high resistance of spinel $MgAl_2O_4$ can be contrasted with the ease of amorphization of forsterite Mg_2SiO_4 and enstatite $MgSiO_3$ [11, 12]. The replacement of Al by Ti in spinel also makes it easily amorphizable, due to the covalency in the Ti–O bond as discussed above: the high resistance of spinel $MgAl_2O_4$ has been contrasted with the relative ease of amorphization of geikelite $MgTiO_3$ [28]. Finally, the same effect is seen when Al is replaced by Ge in $MgAl_2O_4$, resulting in readily amorphizable Mg_2GeO_4 [42], because it lends this compound the possibility to form a stable disordered covalent network due to the covalency in the Ge–O bonding.

• The topologically identical pyrochlores $Gd_2Ti_2O_7$ and $Gd_2Zr_2O_7$ show striking differences in resistance to amorphization, with $Gd_2Ti_2O_7$ readily amorphizing, while $Gd_2Zr_2O_7$ cannot be amorphized even at 25 K. Moreover, progressive increase of the Zr content x in $Gd_2(Zr_xTi_{2-x})O_7$ from 0 to 2 results in a consistent increase in resistance [29]. This effect is important since both pyrochlores are considered potential waste forms, and the remarkable resistance of zirconate pyrochlore gives it an advantage over the titanate one. The origin of the striking difference in resistance between the two pyrochlores has remained unknown, but can be readily explained in the picture proposed here.

In fact, this example gives a particularly good illustration of the competition between the long-range and short-range forces. The radiation cascade created in $Gd_2(Zr_xTi_{2-x})O_7$ contains both Zr–O and Ti–O 'phases'. The former has a higher degree of ionicity, whereas the latter has substantial covalency, as discussed above. Changing x results in changing the contributions of the long-range ionic and short-range covalent forces, coming from Zr–O and Ti–O phases, respectively. Hence, in the proposed picture, the resistance of $Gd_2(Zr_xTi_{2-x})O_7$ is expected to increase with Zr content and decrease with Ti content, exactly as is seen experimentally.

• A similar example involves the dramatic difference in resistance between $Er_2Ti_2O_7$ and $Er_2Zr_2O_7$, with $Er_2Ti_2O_7$ being readily amorphized while $Er_2Zr_2O_7$ remains crystalline even at very high doses [7, 8]. Just like for Gd-based pyrochlores, this difference in resistance can be explained by noting the presence of the damage-stabilizing titania phase (due to the covalency in the bonding) in amorphizable $Er_2Ti_2O_7$.

• Another similar example is provided by the comparison of ABO pyrochlores with B = Zr, Hf and Sn. First, note that while SnO_2 is readily amorphized by irradiation, HfO_2 is more resistant [86] (that ZrO_2 is known to be highly resistant was already discussed above). Recent experiments indicate that $La_2Zr_2O_7$ pyrochlore is more resistant than structurally identical $La_2Hf_2O_7$ pyrochlore, which, in turn, is considerably more resistant than $La_2Sn_2O_7$ pyrochlore [111]. Consistently with the proposed criterion of resistance, the electronic density maps reveal that the covalency of the B–O bond increases in the order Zr–O, Hf–O, Sn–O in these pyrochlores [112]. Using the same arguments, the higher resistance of $Gd_2Sn_2O_7$ relative to $Gd_2Hf_2O_7$ [45] can be explained.

• It is found that phosphates such as $LaPO_4$, $PrPO_4$, $GdPO_4$, $LuPO_4$ can be readily amorphized at room temperature [14, 22], which in the proposed picture is explained by the substantial covalent contribution to the P–O bonding. At the same time, these phosphates are more resistant than the structurally similar or identical orthosilicates $ZrSiO_4$ and $ThSiO_4$ [14, 22]. The P–O bond is about as covalent as the Si–O bond, but the difference in resistance arises because the ability to form a three-dimensional covalent network is reduced in phosphates relative to silicates due to the presence of the 'double' bond in these phosphates [113]. Therefore barriers to recrystallization are reduced in these phosphates relative to silicates, explaining their higher resistance to amorphization. This example suggests that the network-forming ability, in addition to the bonding type, may be important for resistance: molecular units (PO_4 in the example above) contain P–O bonds with significant

covalency, but do not connect as efficiently in the three-dimensional network as silicates. In addition to the phosphates above, $AlPO_4$, $CePO_4$, $Ca_5(PO_4)_3F$, $FePO_4$ and $GaPO_4$ are readily amorphizable as well [115, 114, 116].

• The discussion of experimental data need not be limited to oxides, which the waste forms are. A quick survey of data reveals that resistance to amorphization of semiconductors and other technologically important materials can also be explained by the proposed criterion.

It has been recently found that GaN and ZnO are considerably more resistant to amorphization than GaAs, GaSb, InSb and Si [54, 55, 119]. Similarly, Si_3N_4 is highly resistant to amorphization, whereas SiC is readily amorphizable [31, 32, 94, 96]. Note that SiC has less structural freedom than Si_3N_4, and therefore is expected to be more resistant according to the topological criterion that predicts higher resistance of structures that are more constrained [31, 32]. Attempts have been made to reconcile this apparent contradiction, noting that in SiC, chemical disorder, in the form of Si–Si and C–C chains, assists the amorphization [117, 118].

The origin of these differences in resistance becomes easier to understand using the same arguments for resistance to amorphization as for other materials discussed above. In comparing GaN and ZnO versus GaAs and GaSb or Si_3N_4 versus SiC, one notes that bond ionicity can be compared quite reliably between these materials using empirical electronegativity values, because N, F, Cl and O have the highest values of electronegativity of all elements, higher than 3 in the Pauling scale [97]. In these examples, one group of materials has a highly electronegative element (N and O in the examples above), while the other does not, and hence is considerably more ionic in its bonding. In the proposed picture, this is expected to result in higher resistance to amorphization, in agreement with experimental results. The same arguments can be used to explain the high resistance, measured recently, of AlN [120, 56], ZrN [121] and CaF_2 [122], together with the previously known examples such as those of LiF, BaF_2, NaCl, KCl, KBr and other materials [86]. In addition to having highly electronegative elements, the high ionicity of some of these binaries is confirmed by quantum-mechanical calculations [125]. At the same time, strong covalent bonding, as found by quantum-mechanical calculations [125], explains why GaAs, GaSb, InSb, AlAs, SiC, AlP, GaP, InAs, Si, Ge, C and other materials are readily amorphized [86].

I have not discussed a distinct class of materials, metals. Normally, pure metals do not 'amorphize' like the materials discussed above, by readily supporting permanent 'radiation cascades' (see, for example, the comparative study in [67, 68]), but can support other defects such as point defects and dislocations. In MD simulations of radiation damage in metals, high mobility of defects is seen [63]. This suggests that the high mobility makes it possible to efficiently recover from the damage. Although the interatomic forces in metals are short ranged due to the screening by electrons, the barriers associated with the relative motions of atoms are small relative to those in the amorphizable materials discussed above. This promotes the 'recrystallization', driven by the need to pack atoms in the ordered close-packed metal structure, with surrounding crystal providing a template for ordering. Some metallic alloys, on the other hand, can be amorphized (see, for example, [123, 124]). Note the similarity with metallic glasses: pure metals do not form glasses while some metallic alloys do, provided that the ratio of atomic radii is large enough (in the glass area, this is called the 'confusion principle' [126]).

4.2. Summary

Table 1 lists the materials discussed above, and provides a general trend of varying resistance with chemistry. It should be stressed that the division into 'resistant' and 'amorphizable'

Table 1. Examples of materials showing different resistances to amorphization. See section 4.1 for a detailed discussion and section 4.2 for a summary and the basis for the classification into resistant and amorphizable materials.

Amorphizable materials

1–37: SiO_2 (2 polymorphs), $MgSiO_3$, Al_2SiO_5 (3 polymorphs), Fe_2SiO_4, Mg_2SiO_4, $ZrSiO_4$, $MnSiO_3$, $CaSiO_3$, $CaTiSiO_5$, $Ca_3Al_2(SiO_4)_3$, $Mn_3Al_2(SiO_4)_3$, $NaFeSi_2O_6$, $CaMgSi_2O_6$, $LiAlSi_2O_6$, $BaTiSi_3O_9$, $NaAlSi_3O_8$, $CaAl_2Si_2O_8$, $KAlSi_2O_6$, $Ca_2(Al, Fe)_3(SiO_4)(Si_2O_7)(OH)$, $Fe_3Al_2(SiO_4)_3$, $Ca_3Fe_2(SiO_4)_3$, $Ca_2Mg_5(Si_8O_{22})(OH)_2$, $Al_3Mg_2(Si_5AlO_{18})$, $REE^{3+}FeBe_2Si_2O_{10}$, $KAl_2(Si_3Al)O_{10}(OH)_2$, $KMg_3(Si_3Al)O_{10}(OH)_2$, $LiNa_2K(Fe, Mg, Mn)_2Ti_2Si_8O_{24}$, $3Al_2O_3 \cdot SiO_2$, $Mg_3Al_2Si_3O_{12}$ [11, 12, 16], $K(Mg, Fe)_3(AlSi_3O_{10})(OH, F)_2$, $K(Li, Al)_3(Al, Si)_4O_{10}(OH, F)_2$ [37], $ThSiO_4$ (2 polymorphs), $HfSiO_4$ [26];

38–40: GeO_2 (2 polymorphs) [38], Mg_2GeO_4 [42];

41–61: TiO_2 [9, 27, 95], $Er_2Ti_2O_7$ [7, 8], $CaTiO_3$, $SrTiO_3$, $BaTiO_3$ [15], $Gd_2Ti_2O_7$, $Sm_2Ti_2O_7$, $Eu_2Ti_2O_7$, $Y_2Ti_2O_7$ [19, 20, 29, 48, 51], $Tb_2Ti_2O_7$, $Dy_2Ti_2O_7$, $Ho_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Lu_2Ti_2O_7$ [51], $CaZrTi_2O_7$ (4 zirconolite compositions) [13, 48], $FeTiO_3$, $MgTiO_3$ [17, 28], $BaAl_2Ti_5O_{14}$ [116];

62–64: SnO_2 [86], $Gd_2Sn_2O_7$ [45], $La_2Sn_2O_7$ [111];

65–81: $LaPO_4$, $PrPO_4$, $NdPO_4$, $SmPO_4$, $EuPO_4$, $GdPO_4$, $ScPO_4$, YPO_4, $TbPO_4$, $TmPO_4$, $YbPO_4$, $LuPO_4$ [14, 22], $CePO_4$, $Ca_5(PO_4)_3F$ [114], $AlPO_4$ [115], $FePO_4$, $GaPO_4$ [116];

82–92: GaAs, GaSb, InSb, SiC, GaP, InAs, AlAs, AlP, Si, Ge, C [31, 32, 86, 96, 54, 55, 119, 77, 132];

Resistant materials

93–95: MgO [11, 12, 94, 96], Al_2O_3 [11, 12, 17, 18, 94, 96], $MgAl_2O_4$ [25, 28, 96],

96–102: ZrO_2 [9, 24, 40, 41], $Gd_2Zr_2O_7$ [20, 29], $Sm_2Zr_2O_7$, $Nd_2Zr_2O_7$, $La_2Zr_2O_7$ [20], $Er_2Zr_2O_7$ [7, 8], $Ce_2Zr_2O_7$ [52];

103–105: HfO_2 [86], $Gd_2Hf_2O_7$ [45], $La_2Hf_2O_7$ [111];

106–116: GaN [54], AlN [120, 56], ZrN [121], Si_3N_4 [31, 32, 94, 96], ZnO [55], CaF_2 [122], BaF_2, LiF, NaCl, KCl, KBr [86].

materials in table 1 is not strict. First, one is free to choose what value of D_c or T_c separates resistant materials from amorphizable ones. Second, for the materials listed in table 1, the values of the resistance (quantified by D_c or T_c) were often obtained under different experimental conditions such as with varying ion species, energies and dose rates. Changing these may influence the outcome of an experiment, in that a material may appear to have quite a different resistance under different irradiation conditions [43, 130–133, 136, 134, 135]. Therefore it is not possible to offer an 'absolute' scale of experimental resistance and arrange the materials accordingly.

The division into resistant and amorphizable materials in table 1 is primarily based on experimental data of two types. First, if under the same experimental conditions a material is found to be more resistant than another one, the two materials are placed into 'resistant' and 'amorphizable' groups, respectively. In most cases, the difference in resistance is quite large, as is seen by comparing $MgAl_2O_4$ versus Mg_2SiO_4 (or $MgAl_2O_4$ versus Al_2SiO_5, or $MgAl_2O_4$ versus Mg_2GeO_4), $Gd_2Zr_2O_7$ versus $Gd_2Zr_2O_7$, $Er_2Zr_2O_7$ versus $Er_2Ti_2O_7$, $La_2Zr_2O_7$ versus $La_2Sn_2O_7$, Si_3N_4 versus SiC, GaN versus GaAs etc (see table 1). Second, the division into 'resistant' and 'amorphizable' groups is made for materials that were irradiated under different conditions, but showed large differences in resistance. In this case one can assume that these differences will probably be preserved even if the experimental conditions were the same. For example, materials such as MgO, Al_2O_3, $MgAl_2O_4$, ZrO_2, ZrN, $Gd_2Zr_2O_7$ can be said to be considerably more resistant relative to readily amorphizable silicate and titanate oxides, even though these materials were often irradiated under different conditions.

As a result of such classification, materials within a group may exhibit different resistances, but, except for a relatively small number of cases, these differences are significantly smaller than the differences between materials that belong to different groups. The existence of this small number of cases is the price for keeping the table simple; this, coupled to the limitations stemming from arranging the data obtained under different experimental conditions, suggests that table 1 can be viewed as one of the ways of presenting a general, albeit correct, trend in material resistance. In general, the division of materials into 'resistant' and 'amorphizable' in table 1 reflects a commonly used measure of resistance, namely amorphizability at room temperature. Except for a very few cases, 'amorphizable' materials in table 1 become 'x-ray amorphous' under ion bombardment at room temperature, whereas 'resistant' materials do not, at least at the radiation doses used in the experiments reviewed.

The discussion above, summarized in table 1, includes 116 materials, and this list can certainly be continued on the basis of both existing, as well as the constantly growing resource of experimental data. Note that a significant proportion of materials in table 1 are oxides, including silicates and titanates, as these have been studied and discussed extensively in the literature. It would be interesting to obtain data for materials from other families as well, together with their electronic density maps. Still, the materials in table 1 are diverse enough, in that they are different in chemistry, composition, symmetry group, topological freedom, ratio of ionic radii, density, elasticity, hardness, glass-forming ability, melting points, crystallization temperatures and other properties and parameters. At the same time, the resistance of these materials can be generally explained by one common property, the type of interatomic bonding. One sees that at least for the 116 materials discussed above, the type of bonding appears to be a *sufficient* condition that generally explains the resistance to amorphization. Within a certain family of materials, there may be differences in resistance which might require discussing some additional factors (see section 6); however, such differences are often significantly smaller than the differences between materials belonging to different families (silicate and zirconate oxides, for example). In any case, before these additional factors are discussed, the electronic density maps should be analysed first.

The proposed picture of resistance, based on the type of interatomic interaction, provides answers as regards the origins of resistance for many materials. For example, 12 specific questions about the resistance of tens of different materials, listed at the beginning of section 1, are readily answered in the proposed theory (these and other examples have been discussed in detail above). At the same time, this picture also explains the data for which other explanations have been proposed previously (as well as offers reasons why these other explanations may have worked in some cases and failed in others), i.e. is inclusive. This will be discussed in the next section.

5. Correlations of resistance with other properties

It is interesting to consider the issue raised at the beginning of this work, the possible interconnection between several criteria for resistance to amorphization proposed previously, as well as their relation to the picture based on the type of interatomic force.

Two of the criteria discussed in section 2 are topological freedom and glass-forming ability, and these are shown in figure 3. Consider the link in the diagram between the topological freedom and resistance to amorphization, as proposed in the topological model of resistance to amorphization [30–32], together with the link between the type of interatomic force and topological freedom. These links raise a question of whether a material's geometrical structure
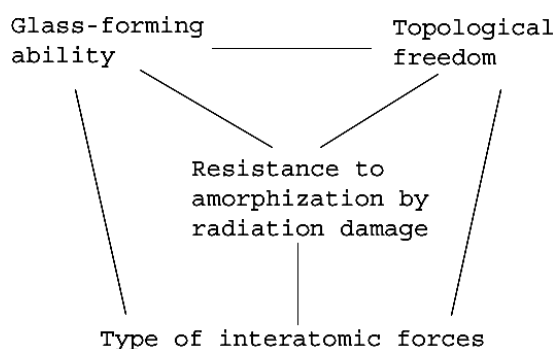
Figure 3. A diagram illustrating the relation between the type of interatomic force, resistance to amorphization by radiation damage, topological freedom and glass-forming ability.

and hence topological freedom is a factor in defining the resistance to amorphization. Do structure and topological freedom, defined by structure, matter in radiation damage?

The experiments discussed in section 4 show that highly resistant materials may have very different structures and topological freedoms. At the same time, materials that are structurally similar or identical (and hence similar or identical in terms of topological freedom), but different in chemistry and hence in bonding type, may show remarkable differences in resistance to amorphization. On the basis of this experimental evidence, as well as the theoretical discussion in section 3, one has to conclude that structure and topological freedom are not defining factors for resistance to amorphization. However, a link between topological freedom and resistance to amorphization may often exist, and could be used to gain quick approximate insights into resistance. I suggest that this link exists insofar as the type of interatomic force is related to the structure: strongly ionic forces, that in the proposed picture favour recrystallization, often also favour highly coordinated structures, while strongly covalent forces, that in the proposed picture act to stabilize the damage, at the same time favour more open low-coordination structures at equilibrium. For binary compounds, for example, Phillips showed that the critical ionicity $f = 0.785$ divides high- and low-coordination structures [85]. Hence a link may often exist between the material's resistance to amorphization and its structural (topological) freedom: the topological theory predicts that highly constrained and lightly constrained structures should have high and low resistance to amorphization, respectively [30–32].

It is interesting to consider why the link between resistance to amorphization and topological freedom breaks down, as discussed in section 4.1. If the proposed picture, which relates resistance to amorphization to the type of interatomic interaction, is correct, this link breaks down when the link between the type of interatomic force and topological freedom breaks down. Note that in the Phillips theory of ionicity, there is an excellent correlation between low- and high-coordination structure with bond ionicity for *binary* compounds [85]. At the same time, the link between resistance to amorphization and topological freedom works for selected binary compounds [30–32]. However, as the discussion in section 4.1 has shown, for ternary, and even for some binary, compounds the link between resistance to amorphization and topological freedom, as well as the link between topological freedom and the type of interatomic force, often fails. At the same time, a criterion of resistance based on the type of interatomic interaction predicts the resistance correctly, including the cases where the topological criterion fails.

Before discussing the previously proposed link between the resistance to amorphization by radiation damage and the glass-forming ability, I make the horizontal link between the

topological freedom and the glass-forming ability. This link, based on the physics of glass, has become apparent from the pioneering works of Phillips [127, 128] who showed that the 'ideal' glass should have a well-defined average coordination number $\langle r \rangle = 2.4$, that corresponds to the balance between overconstrained and underconstrained structure, with the former resulting in the recrystallization of a 'frustrated covalent network' [127, 128], and thus inhibiting glass formation, and the latter leading to decomposition into underconnected chains. This theory has since enjoyed most success in predicting numerous properties of glasses. It is interesting that some time after advancing his theory of glasses, Phillips also discussed the importance of ionicity for the stability of radiation-induced point defects [119] in binary compounds.

To conclude the discussion of figure 3, I make the link proposed to exist [11, 12] between glass-forming ability and resistance to amorphization by radiation damage (see figure 3). Like the correlation with the structural freedom, this link may or may not exist. Many materials that are readily amorphized by radiation damage either do not form glasses by liquid quenching at all, or are bad glass formers. For example, Si, Ge, complex titanate oxides and other materials are overconstrained according to Phillips theory ($\langle r \rangle > 2.4$), and indeed do not form glasses by conventional liquid quenching [88]. Other materials, including complex silicate and titanate oxides, may not form glasses because they phase decompose, and yet all these materials are amorphized by radiation damage relatively easy. One may wonder why this is so. The radiation damage process and glass quenching are remarkably different in terms of timescales and length scales. As a result, in radiation damage, the thermal energy is dissipated quickly enough to inhibit crossing barriers to recrystallization and allow the formation of a locally disordered covalent network, even if it is 'frustrated' in the Phillips sense and hence should not form glass easily. On the other hand, during a much slower liquid quench, the system can sample the phase space much more efficiently, and hence one can describe a glass-forming system simply as a network that should obey the balance between degrees of freedom and constraints, regardless of the details of the system preparation process. This was a starting point of Phillips theory [127, 128]. In this theory, an overconstrained system should recrystallize in order to satisfy the balance between degrees of freedom and constraints, and, unlike in radiation damage, it is assumed that it is able to cross barriers to recrystallization during liquid quenching.

Figure 3 illustrates that three different properties, resistance to amorphization by radiation damage, glass-forming ability and topological freedom (structure), are related to the nature of the interatomic forces. Therefore it should not be surprising that the three properties may correlate with each other, but whereas the resistance to amorphization by radiation damage may or may not correlate with glass-forming ability and topological freedom, there is an excellent correspondence between glass-forming ability and topological freedom, measured by $\langle r \rangle$ [127, 128].

In addition to glass-forming ability and topological freedom, one can ask whether other proposed criteria of resistance can also be related to the picture in which resistance is generally defined by the type of interatomic force. For example, it has been proposed in several models that the ease of accommodating cation disorder, which increases as the ratio of cation radii decreases, results in the increase of resistance to amorphization of an ABO compound (see section 2.1). Recall that in the proposed picture, resistance increases with ionicity of bonding. On the other hand, a larger ratio of cation radii has been related to smaller resistance (see section 2.1). Note that increased covalency (which reduces resistance in the picture proposed here) is sometimes associated with smaller ionic 'radius' and hence larger ratio of cation radii. In this sense, the picture of resistance based on the type of interatomic interaction is inclusive of the models that relate resistance to cation radii ratio. However, it should be borne in mind that for bonds with appreciable covalency, the ionic model of a solid and hence ionic radii lose

their meaning [75]. For example, the analysis based on the ratio of cation radii of the resistance of ABO compounds with B = Ti, Sn (see section 2.1) and other elements with a considerable covalent contribution to the bonding might not be adequate. This is because ionic radius/size is not defined when there is appreciable covalency in the bonding, since there is no spherical symmetry of the electronic density. This makes the ionic picture of a solid (and hence the values of cation radii) inadequate, as is discussed in detail in [75].

Finally, it is possible that the links of the proposed picture with other models and criteria, discussed in section 2, might exist in some cases as well. One therefore concludes that the picture of resistance based on the type of interatomic force is inclusive, in that it can be related to the previously proposed theories and models.

6. Discussion of possible future work

On the basis of the picture of resistance to amorphization by radiation damage discussed above, one can discuss what the future directions of research might be. One obvious direction is quantifying the resistance of materials using electronic density maps obtained either experimentally or from quantum-mechanical calculations. First, one needs to obtain these maps for a larger range of materials than are currently available. Second, one needs to select the manner of quantifying resistance on the basis of the electronic density maps. A few possibilities exist in quantum-mechanical calculations, including calculating Born effective charges, Mulliken populations, dynamical charges and other quantities [125, 129]. It may appear that using several sets of differently defined quantities can be appropriate for comparison with the experimental data on resistance and for prediction of experimental results.

It should be stressed that the inability to form a covalent network does not always imply that a material should be resistant to amorphization by radiation damage. In other words, there may be other factors that may reduce a material's resistance. This is not surprising, given the extreme nature of processes involved in radiation damage, and is behind the fact that among the materials considered above, only about 20% can be described as resistant to amorphization, i.e. as capable of recovering efficiently from the damage (see table 1). I have tried to suggest that regaining coherence with a crystalline lattice is significantly promoted in a system with long-range (ionic), relative to short-range (covalent), forces, but it does not guarantee that this will always be the case under given conditions. For example, a material's resistance can decrease due to the electronic defects (neglected in the discussion above) that appear at high energies, and stabilize the damaged structure in materials that are highly ionic and resistant to amorphization at lower energies [136]. Next, chemical demixing in a radiation cascade can cause phase decomposition, inhibiting the recrystallization process in an otherwise resistant material (for example, in the formation of nitrogen bubbles in GaN; see [137]). This may include a case where a material (a binary oxide, for example) can support more than one charge state and can undergo radiation-induced decomposition into differently charged states. Finally, the large ratio of cation sizes in, for example, ionic ABO material can inhibit recrystallization (see [20]) and affect the resistance, similarly to the 'confusion' principle used in preparing metallic glasses [126]. A more detailed consideration of these and possibly other relevant points should also be the next step in these studies.

Computer simulations of radiation damage may provide more insights into resistance to amorphization. In the MD simulations, the outcome of the simulation of a radiation damage event depends on the empirical potential. This potential often has electrostatic charges to emulate the ionicity of bonding. In addition, even for materials with very high ionicity, the potential also contains short-range 'bonding' interactions in order to stabilize the structure (the weights of the long-range and short-range interactions in the total Hamiltonian are normally

fixed by the need to tailor these interactions to the properties at equilibrium). The 'bonding' interactions are taken in, for example, the popular Buckingham form, and often have the minimum of energy at the short-range distances. These interactions may limit the atomic mobility needed for the recrystallization of an ionic material in radiation damage simulations. In fact, the resulting damage necessarily reflects the interplay between the short-range covalent and long-range ionic contributions, and these are often fixed by the need to emulate conditions at equilibrium. Developing empirical models with properly accounted for ionic and covalent components may help in understanding the progressive change of the resulting damage in the structure. This could be done by varying the ionic long-range and covalent short-range contributions and simulating radiation damage events in each model.

Other computer simulation techniques such as those allowing one to calculate the energy cost of cation disorder [7–10, 46] should continue to make interesting predictions concerning resistance to amorphization. Finally, another possibility for computer simulations may be employing recently developed techniques that enable one to characterize the potential energy landscape using interatomic functions (see, for example, [138]). If short-range and long-range forces compete in creating an energy landscape with a certain distribution of the number of minima and barrier heights, these techniques may allow one to characterize the energy landscape in detail for each set of differently weighted contributions of long-range and short-range forces. Such analysis may be useful for providing further insights into the issue of resistance to amorphization. For example, it may allow one to relate the critical amorphization temperature to the details of the potential energy landscape.

7. Summary

I have reviewed ideas and concepts that have been put forward in order to help with understanding the issue of resistance to amorphization by radiation damage. Whereas it might not be a full account of the state in the field, I hope that it can help the reader to get a better feel for research in this area. I have tried to suggest that the type of interatomic force may hold the key to the problem, because it defines how atoms interact and rearrange in a solid. The ability to form a covalent network leads to damage stabilization and makes a material amorphizable by radiation damage. High ionicity, on the other hand, results in higher resistance. I have proposed that on a more detailed level, the resistance to amorphization of a complex (non-metallic) material is defined by the competition between the short-range covalent and long-range ionic forces.

The review of experimental data suggests that the proposed criterion can generally explain the resistance to amorphization of 116 materials. While this provides strong support to the proposed theory, the role of other possible mechanisms that can affect resistance needs to be investigated further. At the same time, the proposed picture of resistance allows one to make some important predictions as regards durability of waste forms and other materials exposed to irradiation.

Finally, I have discussed how the proposed picture is related to ideas put forward previously and suggested a few possible issues to be addressed by means of theory, experiments and computer simulations in order to help us understand the problem better.

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