Electron anions and the glass transition temperature

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Properties of glasses are typically controlled by judicious selection of the glass-forming and glass-modifying constituents. Through an experimental and computational study of the crystalline, molten, and amorphous [Ca$_2$Al$_2$O$_5$]$^{2+}$($e^-$)$_2$, we demonstrate that electron anions in this system behave as glass modifiers that strongly affect solidification dynamics, the glass transition temperature, and spectroscopic properties of the resultant amorphous material. The concentration of such electron anions is a consequential control parameter: it invokes materials evolution pathways and properties not available in conventional glasses, which opens a unique avenue in rational materials design.

Significance

Electrides are ionic materials in which electrons act as anions. Solvated electrons in ammonia are one of the early known examples of such anions in liquids. Electron anions in crystalline materials have previously been shown to dramatically alter their electronic properties, for example, to turn an insulator into a superconductor with minimal changes in the structure and stoichiometry. We show that electron anions modify the disordered glass network by creating highly mobile weak links, thus fundamentally altering the thermodynamic and electronic properties of the network and enabling a new design paradigm for amorphous materials.

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One of the key challenges in materials design is identification of degrees of freedom that ensure robust control of the properties of interest. Small changes in composition of crystalline materials can lead to large changes in their electronic properties, such as optical absorption and electrical conductivity (1). Similarly, a small concentration of (co)dopants in amorphous materials can be used to control their optical properties (2, 3). Glass properties are typically controlled by varying composition or processing conditions (4). However, delicate control of viscosity and glass transition temperature in multicomponent materials ($T_g$) has remained elusive due to the collective origin of these properties. Substitution of atomic anions with electron anions in materials to form electrides (5, 6) introduces an additional degree of freedom. Here we demonstrate that electron anions dramatically change dynamics of atoms in an inorganic amorphous material, which strongly affects its $T_g$. Extending the concept of electron anions to other amorphous materials would provide a powerful instrument for the design of glasses with finely tuned characteristics.

Calcium aluminates (CA), composed of CaO and Al$_2$O$_3$, represent a common family of oxide glasses. Whereas pure Al$_2$O$_3$ is a poor glass former, blending it with CaO leads to the formation of stable glasses composed of AlO$_4$ tetrahedra with strong and directional covalent bonds instead of nondirectional ionic bonds in bulk Al$_2$O$_3$ (7). In contrast, Ca-O bonds retain their ionic character; they are weaker than Al-O bonds and lack a preferred orientation, which enables motion of the AlO$_4$ tetrahedra relative to each other. Hence, the $T_g$ of stoichiometric CA systems decreases by ~50 K as the CaO content increases from 57 mol% to 70 mol% (Fig. 1). This relatively narrow interval of $T_g$ variation with composition is typical of multicomponent glasses (8, 9). The $T_g$ for stoichiometric [Ca$_2$Al$_2$O$_5$]$^{2+}$($e^-$) (C12A7) is in line with the general trend for CA systems (~830 °C). Conceptually, $T_g$ of a glass network can be further modified by introducing weak links. For example, $T_g$ of CA systems can be modified by addition of CaF$_2$, which reduces the number of Al-O-Al bridges between the tetrahedral structural elements and decreases their viscosity. As a result, $T_g$ decreases by ~75 K at a mole fraction of 20% CaF$_2$ (10). Similar effects can also be achieved by replacing lattice oxygens with other anions such as H$^-$ and OH$^-$ (11). Processing C12A7 in a reducing environment leads to replacement of clathrated oxygens with electrons (12, 13), forming [Ca$_2$Al$_2$O$_5$]($^{2+}$)($^{3-}$)$_{1-x}$(e$^-$)$_x$, referred to as C12A7 electrode (C12A7:e$^-$) due to electrons functioning as anions (5, 14, 15). In crystalline C12A7:e$^-$, the electrons occupy the cage conduction band (CCB) states associated with the lattice cages (16, 17), leading to polaron-type conduction at $x < ~0.5$ and metallic conduction at $x > 0.5$ (13, 16). The exceptionally low work function of crystalline C12A7:e$^-$ (2.4 eV) (18) is used in electron field emitters (19, 20), field-effect transistors (21), resistive memory (22), and enhancement of catalytic activity for ammonia synthesis (23). Amorphous C12A7:e$^-$ (a-C12A7:e$^-$) also has a low work function (24), providing a host of new applications and technologies at the industrial scale. Whereas the structure and electronic properties of the crystalline C12A7 have been extensively investigated, there is a handful of experimental and computational studies of a-C12A7:O$^-$ (25, 26) and a-C12A7$^-$ (27, 28), focused on the structural properties of a-C12A7. However, the effects of nonstoichiometry have remained elusive.

Electrons, even at low concentrations (N$_e$), lead to dramatic changes in the $T_g$ values (Fig. 1): for $x = 0.095$ (N$_e$ = 2.2 x 10$^{20}$ cm$^{-3}$) the $T_g$ drops by 50 °C to ~770 °C and for $x = 0.475$ (N$_e$ = 1.1 x 10$^{21}$ cm$^{-3}$) it decreases by over 40 °C more, to ~725 °C, for a total change of over 90 °C. These data support a recent report where only one $T_g$ value for an electron-rich C12A7 was reported (29). The change in $T_g$ in this CaO-Al$_2$O$_3$ system induced per mole of electron anions is a factor of 6 greater than that induced per mole of F$^-$. Such a dramatic $T_g$ effect is remarkable and, if understood and controlled, promises the development of a fundamental class of multicomponent amorphous materials in which $T_g$ is responsive to small compositional changes.

The experimental results raise two questions: (i) Why does the effect of oxygen deficiency outweigh the effect of CaO/Al$_2$O$_3$ ratio? And (ii) can it be realized and harnessed in other systems? Here we reveal atomic-scale mechanisms of how electron anions in C12A7 alter the lattice dynamics in the crystalline and molten phases, ultimately affecting the $T_g$, structure, and electronic properties of this material. To reveal the distinctive role of the...
electron anions in the glass formation process and the resulting properties, we conducted ab initio (density functional theory) spin-polarized molecular dynamics (AIMD) simulations, in which crystalline \([\text{Ca}_2\text{Al}_2\text{O}_6]^{28}\) (\((\text{O})_{24}\text{Ca}(\text{e})_{4}\)) (for \(x = 0\) and \(x = 1\)) was subjected to heat-pressures–quench treatments mimicking the experimental procedure. Analysis of the electronic properties and structure evolution with \(T_e\) and \(N_e\) reveals characteristic structural and spectroscopic signatures associated with the electron anions and allows us to (i) explain the strong dependence of the \(T_g\) on \(N_e\) and (ii) propose the formation mechanism that may hold for other materials containing electron anions.

Methods

Experimental Details. Stoichiometric C12A7 can be readily converted to a glass form by a conventional melt-and-quench method. Whereas the chemical composition of C12A7 electrode (C12A7:e) differs from that of stoichiometric C12A7 by only 3% of the oxygen content, C12A7:e– glass could not be obtained by the same method due to very fast crystallization of the melt. To overcome this problem, we designed a process that ensures C12A7:e– cooling at a shorter timescale than crystallization. This result was achieved with the help of the twin-roller apparatus shown in Fig. S1 and described in detail elsewhere (29). The sintered powder of the polycrystalline C12A7:e– was melted in the controlled O2 atmosphere with the gas pressure \((p_0_2)\) of \(-10^{23}\) atm, using a floating zone furnace with lamp heaters. The melt was dropped into the space between the rotating twin rollers. The low \(p_0_2\) (\(10^{23}\) atm) atmosphere was kept around the twin roller apparatus to prevent the oxidation of the melt and the formation of glass flakes. The amorphous nature of the resulting samples was confirmed by X-ray diffraction experiments and by electron diffraction experiments carried out for a selected part of the material in the transmission electron microscopy mode. The electron concentrations and the chemical compositions of the resulting glasses were determined by ionic diffraction analysis and X-ray fluorescence, respectively. The Ca:Al atomic ratio in the samples was 47 ± 1.5:3 ± 1, which is almost the same as the Ca:Al ratio in crystalline C12A7. The glass-transition temperature \((T_g)\) was determined by differential thermal analysis (DTA). Before conducting the DTA measurements, the sealed glass was annealed at \(-650\) °C (heating rate was 20 K/min) in the ambient atmosphere to alleviate quenching-induced stress. The resulting glass flakes were sealed into a thin wall SiO2 glass tube to suppress the oxidation during heating.

Computational Details. Models of the amorphous stoichiometric (a-C12A7:O2–) and electrode (a-C12A7:e–) C12A7 were obtained from the corresponding crystalline forms, using the melt-and-quench approach. The initial crystalline phases were represented using a cubic unit cell \([\text{Ca}_2\text{Al}_2\text{O}_6]^{28}\) (\((\text{O})_{24}\text{Ca}(\text{e})_{4}\)) for the electrode and \([\text{Ca}_2\text{Al}_2\text{O}_6]^{28}\) (\((\text{O})_{24}\text{Ca}(\text{e})_{4}\)) for the stoichiometric C12A7, respectively, and the lattice constant \(a_0 = 12.0\) Å. Their geometrical parameters and electronic properties were in good agreement with the experimental data (30, 31). To separate the effect of the electrons as pseudoanionic species from the effect of the stoichiometry (i.e., the relative content of Al2O3 and CaO components), we conducted simulations on the C12A7 “pseudo-electride,” in which the excess electrons are replaced by a homogeneous electron gas with the density \(\rho\) corresponding to the total charge of \(e^{-}\) per cell: \([\text{Ca}_2\text{Al}_2\text{O}_6]^{28}\) (\((\text{O})_{24}\text{Ca}(\text{e})_{4}\)).

Atomic trajectories were simulated in the microcanonical (constant particle number, volume, and energy) ensemble, using the Vienna Ab Initio Simulation Package (VASP) 5.2.12 (32), the exchange-correlation functional by Perdew–Burke–Ernzerhof (PBE) (33), projector augmented wave (PAW) pseudopotentials (34, 35), and a time step of 0.5 fs. Each molecular dynamics (MD) simulation begins with 4.0 ps of isochoric heating to a target temperature \(T_{\text{max}}\). After equilibration, the supercell was isotropically compressed in four equal decrements over 16.0 ps until the target density was reached (2.95 g/cm3 and 2.79 g/cm3 for C12A7:e– and C12A7:O2–, respectively). Then, the systems were quenched by uniformly scaling atomic velocities so kinetic energy was decreased by 5.0 eV every 2.0 ps until a temperature of \(-100\) K was reached. Finally, the total energies of quenched systems were minimized with respect to the fractional coordinates of all atoms and the cell parameters. Dielectric functions were calculated for selected prereleased systems, using VASP 5.4.1 and the HSE06 hybrid functional (36).

Trajectories were visualized using the VMD program (37), and extracted coordinates and band-projected charge densities were visualized using the VESTA program (38). Cyclic structures were identified using R.I.N.G.S 5.1.25 (39), and partial charges were calculated using the Bader method (40). Raman spectra, including resonance effects, were calculated for simplified models of localized electron anions, using NWChem 6.5 (41). Further details of simulation parameters and data analysis are included as Supporting Information.

Results and Discussion

The electronic structure changes in C12A7 after heating and quenching were characterized using the one-electron energies associated with the top of the 2p valence band (VB) and several lowest states of the CCB. Two representative cases for C12A7:e– (\(x = 1\)) are shown in Fig. S2. For the maximum temperature \((T_{\text{max}})\) of 1,910 K, the crystalline C12A7:e– did not melt within the simulation time. No significant fluctuations occurred in the energy levels with one notable exception at \(-7\) ps into the MD run where the energy of one of the occupied states decreased by over 1 eV due to the formation of a defect center in which two electrons were trapped between two Al species—an Al(2e–)Al center. In contrast, at \(T_{\text{max}} = 2,650\) K, energies fluctuated until well into the quenching stage of the simulations. Charge distributions and pairwise correlation functions (Figs. S3 and S4) indicate that the system melted and then solidified during this MD run, whereas the four electrons became localized in two defects centers: Al(2e–)Al and Al(2e–)Ca. The solid-to-melt phase transition and quenching are discussed further in Supporting Information.

Similar simulations were conducted for seven values of \(T_{\text{max}}\). The resulting total energies and mass densities are compared in Fig. 2A. For \(T_{\text{max}} > 2,400\) K the calculated density of the material was \(-15\%\) higher than that for \(T_{\text{max}} < 2,400\) K. Although atypical for a glass, which is typically less dense than the corresponding crystalline material (4, 42), it is consistent with the density difference between the amorphous and crystalline C12A7:e– observed experimentally (29), which we attribute to the collapse of the lattice framework and loss of the framework cage space. The topology change is evidenced by the loss of the six-membered Al-O-Al-O-Ca-O rings (Fig. 2A). Inset connecting the neighboring cages in the crystal and the appearance of other types of six-membered rings, the corresponding changes of the four-membered ring distribution are shown in Fig. S5. The density correlates with the internal energy of the material: More compact structures correspond to larger deviations from the crystalline C12A7:e– and are less thermodynamically stable (Fig. 2A).

The electron anions in quenched C12A7:e– localize in three types of defects; the corresponding one-electron energies relative to the band edges are shown in Fig. 2B and the local structure of...
electron centers in Fig. 2C. Bipolarons, i.e., pairs of spin-coupled electrons localized in two neighboring distorted cages, closely resemble pairs of electron polaron in crystalline C12A7e− (16, 27). The spin-up and spin-down electrons have similar charge density distributions and indistinguishable one-electron energies, located within several 10ths of an electronvolt from the conduction band (CB) minimum. The formation of bipolarons is suppressed if the lattice cages deform or collapse. Deformation results in Al(2e−)Ca centers: cage-like structures with two electrons localized between a 3-coordinated Al3+ ion and one or more Ca2+ ions. The corresponding one-electron energies are approximately in the middle of the quenched C12A7e− band gap. Alternatively, Al(2e−)Al centers (Fig. 2C) are formed either due to the lattice collapse at high T_{\text{max}} or, at low T_{\text{max}} via local deformation of an Al–O–Al angle from ~140° to ~70°. The latter mechanism does not necessitate melting of the lattice framework; furthermore, it may provide an opportunity for manipulating glass formation by varying pressure (43). In both cases two Al3+ ions are brought to 2.6–2.8 Å from each other, which creates a deep potential well that traps two electrons. The post-AIMD electronic structure calculations using a hybrid density functional resulted in the same ordering of the defect energy levels and similar electron density distributions. Details of the electronic structure are shown in Fig. S6.

These two-electron defects are fully consistent with the observation that less than 1% of electron anions give rise to unpaired spins, as detected by electron spin resonance spectroscopy (29). Indeed, in Al(2e−)Ca and Al(2e−)Al the spatial distributions of the spin-up and spin-down electrons coincide. In contrast, spin-up and spin-down electrons in bipolarons occupy different regions of space and can become further separated from each other in the process of thermal treatment. Because (bi)polarons are a minority defect (Fig. 2B), the concentration of unpaired spins is low.

According to our statistics, bipolarons are formed if T_{\text{max}} is below or near the melting temperature (T_{\text{m}}), whereas Al(2e−)Ca centers appear if T_{\text{max}} is close to T_{\text{m}} or above it. In contrast, the Al(2e−)Al centers form at both low (1,900–2,200 K) and high (>2,550 K) values of T_{\text{max}}. Their formation at T_{\text{max}} ~ T_{\text{m}} appears to be suppressed in favor of bipolarons and Al(2e−)Ca centers.

Cross-correlated analysis of the thermodynamic properties of quenched C12A7e−, atomic trajectories, and electron charge trapping reveals the microscopic origin of the effect of electron anions on T_{\text{g}}. Fig. 3A shows the atomic speed of individual atoms in C12A7e− and C12A7O2− averaged over 2-ps intervals, as a function of temperature during the quenching stage. At high temperatures all ions are mobile, with stronger-bonded AlO units forming near 1,900 K, indicated by the rapid slowing of Al and O species. Glass formation temperature is determined by weaker bonds involving Ca, O, and electron anion species. At 1,100–1,300 K atomic diffusion continues in C12A7e−, whereas it is negligible in C12A7O2−. This is consistent with the temperature dependence of the heat capacity (C_v): The electrode undergoes a phase transition at ~1,150 K, whereas the same transition in C12A7O2− occurs at higher temperatures, peaking near 1,250 K (Fig. 3B). We adopt these temperatures as the T_{\text{g}} values for the C12A7e− and C12A7O2−, respectively, and note that (i) these C_{\text{v}} peaks occur at the same temperature as the cessation of Ca and O diffusion and (ii) the difference between them (~100 K) is very close to the observed difference. The relationship between T_{\text{g}} and electron anions was further tested by replacing them with a homogeneous static charge distribution (\rhõ); no corresponding decrease in T_{\text{g}} was observed (Fig. 3B and Fig. S7).

The atomic scale events occurring in quenched C12A7e− are illustrated in Fig. 3C and D. Dynamics of the electron anions are illustrated in Fig. 3C (T_{\text{max}} = 2,650 K), where black circles mark Al atoms that trap electrons and Q_A is the amount of the electron charge summed over all Al species. As the temperature of the system decreases to below 1,500 K, only three Al ions are associated with these electrons. Similarly, variations in Q_A become small at T < 1,200 K, indicating that electron transfer...
between Al and Ca species as well as between Al and remnants of the lattice cages ceases at this temperature.

Although diffusive motion of Al ceases at \( \sim 1,900 \) K in both C12A7: e\(^{-} \) and C12A7: O\(^{2-} \), Al\(^{3+} \) ions contribute to the lattice dynamics until the system temperature approaches \( T_g \). Fig. 3D shows the interatomic distance between a selected pair of Al\(^{3+} \) ions during the quench stage (\( T_{\text{max}} = 2,650 \) K). At high temperature the distance between these atoms oscillates in the vicinity of 3.5 Å. However, at \( \sim 9 \) ps into the simulation run (\( T \sim 1,500 \) K), the distance between these atoms rapidly increases to over 4.0 Å and then rapidly decreases to 2.7 Å. This structural rearrangement results in the formation of an Al(2e\(^{-} \))Al center; the signature of this process is also visible in Fig. 3C: The amount of electron charge trapped by Al ions increases sharply at the same time as the Al–Al distance decreases. Furthermore, at \( \sim 12 \) ps the Al–Al distance increases to \( \sim 4 \) Å for about 2 ps before decreasing again. This event is accompanied by a simultaneous decrease and then, 2 ps later, an increase of the electron charge trapped by Al species.

Analysis of the AIMD atomic trajectories and charge density distributions reveals that the formation of Al(2e\(^{-} \))Al and Al(2e\(^{-} \))Ca centers is controlled by the correlated motion of the O\(^{2-} \) and Al\(^{3+} \) ions, whereby the defect formation step is triggered by thermally driven diffusion of an O\(^{2-} \) ion from the first (tetrahedral) coordination shell of an aluminum (Fig. 3D and Fig. S8).

As O\(^{2-} \) ions diffuse through the melt, the coordination number...
of Al$^{2+}$ typically varies between 3 and 5 (Fig. S9). In α-C12A7: O$_2^-$, the Al$^{2+}$ tetrahedral coordination is restored when either another O$^-$ ions diffuses into and occupies the vacant oxygen site or the local structure rearranges from corner-sharing neighboring AlO$_4$ tetrahedra to edge-sharing ones. In contrast, in α-C12A7:e, electron anions preferentially and rapidly localize at the site of the missing O$^-$ to neutralize the exposed charge and restore the tetrahedral environment, leading to the formation of Al(2e$^-$)Al and Al(2e$^-$)Ca centers. Oxygen ions displaced by electron anions coordinate with adjacent metal atoms to form hypercoordinated species such as 5-coordinated Al$^{3+}$ (Fig. S9).

We note that the metal–metal bonding in the M$_1$(2e$^-$)M$_2$ centers (where M$_1$ and M$_2$ are either Al or Ca) is considerably weaker than that in the M$_1$(O$^-$)M$_2$ lattice, forming weak links that disrupt polymeric Al-O structures and increase local mobility in the system, analogous to fluoride or hydroxide anions in conventional glasses. However, in addition to being far weaker than metal–oxygen bonds, electron anions are far more mobile than conventional anions and can be easily displaced. O$^-$ ions diffusing through the lattice react with the M$_1$(2e$^-$)M$_2$ centers and displace the trapped electrons either to the remnants of the C12A7 lattice cages or to other undercoordinated metal sites. Because the electron transfer occurs at a much faster timescale than atomic displacements, such electron transfer and (re)trapping events change the local potential energy surface, i.e., induce forces that accelerate atoms in the vicinity of the defects. Thus, we propose that electron anion transfer events in C12A7:e elevate the local temperature above the global average, thus maintaining the molten phase to lower global temperatures than in α-C12A7:O$_2^-$. Amorphous C12A7:e$^-$ and C12A7:O$_2^-$ have virtually indistinguishable X-ray scattering, neutron diffraction, and infrared spectra. However, the Raman spectra of C12A7:e$^-$ show a narrow resonantly enhanced band peaking at ∼186 cm$^{-1}$ and strongly increasing in intensity as a function of $N_e$ (29). These data provide us with a reference point for the experimental validation of the proposed electronic defects and mechanisms.

To test whether the Raman band is associated with electron anions, we represent the Al(2e$^-$)Al and Al(2e$^-$)Ca defects using linear clusters OAl–AlO (Fig. 4A) and FCa–AlO (Fig. 4B), respectively, denoted for brevity as LM–ML, where M are metals (M = Al, Ca) and L are ligands (L = O, F). These clusters reproduce critical elements of the electron defects in C12A7:e$^-$: electrostatic neutrality, coordination of the metal atoms by ligands L, and localization of two electrons between the metal atoms similar to that in Al(2e$^-$)Al and Al(2e$^-$)Ca. Importantly, these models allow us to isolate the motion of the metal atoms from that of the rest of the system and calculate resonant Raman intensities as functions of $M$–$M$ distances. Both $LM$–$ML$ clusters exhibit a strong Raman peak due to in-phase stretching of the $M$–$M$ bond. As the $M$–$M$ distance increases, the intensities of the peaks increase and their frequencies decrease. The Raman spectra in Fig. 4 show that for the $M$–$M$ distances close to those in the Al(2e$^-$)Al and Al(2e$^-$)Ca centers, the frequencies of both stretching modes are consistent with the observed 186-cm$^{-1}$ peak and the resonant enhancement in LAl–CaL is approximately an order of magnitude higher than that in LAl–AL. We note that because the excited states in the clusters are at higher energies than in the bulk C12A7:e$^-$ system, enhancement in the LAl–AL cluster is underestimated.

The computed imaginary part of the bulk dielectric function Im(ε) for α-C12A7:e$^-$ (9) is compared with the experimentally measured optical absorption spectrum in Fig. 4C. The two intense peaks at 3.2 eV and 4.0 eV are assigned to the transition between the bonding and antibonding orbitals of the Al(2e$^-$)Ca and Al(2e$^-$)Al centers, respectively, whereas the 2.5-eV peak is attributed to the electron transfer from these defects to the gap states associated with the remaining distorted lattice cages. The calculated values are in good agreement with the experimentally observed peaks at 3.3 eV and 4.6 eV and a low-energy tail and consistent with the optical absorption of electron anions in crystalline C12A7:e$^-$ (30), which provides further validation of the proposed electron defect models. Finally we note that the Im(ε) for α-C12A7:O$_2^-$ shows no optical absorption features up to ∼5 eV in complete agreement with the experimental data (29).

Properties of glasses are modified by weakening their continuous polymeric networks with (Fig. 5) dopants that provide ionic nondirectional bonds (e.g., Na$^+$, Ca$^{2+}$) or break and terminate polymeric chains (e.g., F$^-$). Electron anions provide a method to introduce weak links into a glass network, complementing conventional substitution of anions or cations. Furthermore, electron anions are capable of inducing such modifications at lower concentrations than conventional glass modifiers due to their exceptional mobility.

The strong dependence of the $T_g$ on the concentration of electron anions in C12A7 opens up the possibility of fine-tuning the glass formation and processing approaches with small composition changes as long as the origin of this dependence is understood and the underlying mechanisms are controlled. The microscopic model presented here reveals the mechanisms of C12A7 transformation from the crystalline to the amorphous form and explains the dependence of $T_g$ on the concentration of electron anions; it also gives insight into the multiple kinetically controlling processes near $T_m$. We propose that use of electrons as highly mobile anions offers a promising method for attenuating the thermal and electronic properties of amorphous materials formed from oxides of nonreducible metals, facilitating the design of structural and functional glasses and building on the recent discoveries of other stable solid electrides (44–47). Furthermore, the concept of altering network properties via highly mobile weak links, such as electron anions, as opposed to stationary weak links, may have applications in a diverse variety of networks, well beyond the science of noncrystalline materials.

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