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Tellurite Base Glasses – A Structural Study

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Abstract - Tellurite base glasses are most promising glasses now a day. Their potential applications in the field of phonics, lasers ,optical amplifiers, LEDs, and other photonic devices attract researchers . Structural of tellurite with various glass formers is studied.

Key words - Tellurite glasses; tetragonal pyramid; tetragonal bi-pyramid.

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1. TELLURITE GLASSES

1.1 Early studies

Tellurium trioxide (TeO_3) is converted to tellurium dioxide when heated to a temperature at which it becomes a dull red colour (TeO_2). It has been proven that systems with a TeO_2 concentration of more than 90 mol% (the eutectic region of the TeO_2-rich section of the phase diagram) are capable of self-generating glass (Vogel 1994) [1]. Tellurium dioxide is a white crystalline solid that melts at 733 degrees Celsius and doesn't pick up or give off any oxygen when it does so. They made the first substantial addition to the subject since Berzelius's 1834 pioneering work on sodium tellurite (Berzelius 1834) [2], when they discovered that sodium di- and tetratellurite fuse below red heat to make a transparent glass. In 1913, Lenher et al. 1934 examined the chemistry of the so-called metallic tellurites [3]. They discovered that sodium di- and tetratellurite fuse below red heat to make a transparent glass. This investigation also discovered that sodium tellurite dissolves extremely fast in water. This was a very important result (important when considering glass durability). To our knowledge, the first comprehensive research of tellurite glasses was carried out by Stanworth in 1952a and 1952b [4, 5].**Table 1.7** shows the relative electronegativity of a number of network formers, and the investigation was conducted with the premise that Te4+ has an electronegativity in the same ballpark as these other outstanding glass forming oxides. (Stanworth's electronegativity criterion (Rawson 1967) is used to define this property [6].

Table 1: Electronegative characteristics of glass-forming oxides and network modifiers that are efficient (Stanworth 1952). [5]

Element	Pauling electronegativity
Glass network formers	
Te	2.1
B	2.0
Si	1.8
P	2.1
Ge	1.7
As	2.0
Sb	1.8
Glass network modifiers	
Li	1.0
Na	0.9
K	0.8

This is because these glass formers scatter other elements with lower electronegativity, resulting in fewer ionic interactions with oxygen in the network. In order to produce glass, these substances establish strong covalent bonds with oxygen. Zachariasen's requirements for glass formation state that cations in a good glass maker should be surrounded by 3 or 4 anions, and that the bulk of the anions are coupled to two cations, hence this electronegativity-based prediction of glass formation proved useful. The fact that the vast majority of anions are already bonded to two cations led to this hypothesis about glass production. Two of the oxygen atoms in α-TeO_2 are closer to the cation than the other four, unlike in tin oxide, where each cation is surrounded by six oxygen atoms. Each cation in tin oxide is surrounded by eight oxygen atoms. This allows us to think of the structure as a bunch of TeO_2 atoms, rather than some other kind of thing (see the next section for a more detailed discussion of TeO_2 structure, and its relation to the glass network). Thus, it is not reasonable to expect simple glass to develop from TeO2 using the Zachariasen criteria. In addition, it seems that tetrahedral coordination in the pure oxide is impossible because of the huge radius of the Te^{4+} ion (97 pm (Greenwood and Earnshaw, 1995) [7]. After plugging TeO_2's field strength (0.71) into Dietzel's equation for field strength (2.1), we find that it belongs to the intermediate group. Therefore,

TeO_2 belongs to the intermediate-group of elements, as seen above. Zachariasen and Dietzel found that under these unfavourable conditions, glasses may be made using tellurite systems, which are thermally stable. Given what we know about the chemical bonding in TeO_2, Stanworth in 1952b was able to make some informed estimates regarding the properties of tellurite glass. The partial refractive index of oxide MmOn may be estimated using the formula (1.4), where Vo is the volume of glass that includes 1 g.atom of oxygen, N_M is the number of atoms of M present in the glass for every atom of oxygen, and a_M is the partial refractive index of component MmOn.

$$(n-1)V_0=\Sigma\, a_M N_M \qquad \ldots\ldots\ldots(1.4)$$

According to Stanworth's research, the amount of tellurium dioxide that raises the refractive index of glass is determined to be, $a_M \approx 1.93$. Tellurite glasses, Stanworth theorised, would have lower softening points than silicates. For the same reasons, including lower melting points and weaker Te-O bonds compared to Si-O, this also held true for both materials. The melting points were anywhere between 250 and 400 degrees Celsius. The melting of fluorotellurite glasses is ascribed to Stanworth 1952b. The ternary mixture of TeO_2, PbO_2, and ZnF_2 was the key to his success. Heating glasses with ZnF_2 concentrations from 8.2 to 33.2 mol percent in a zirconia crucible resulted in glass formation. These compounds were shown to have higher infrared transmission (extinction coefficient of 0.5 from 1.5 to 5 µm) than oxides (TeO2 with PbO, or BaO, and one of the following: SO3, Li2O, Na2O, B2O3, Nb2O5, P_2O_5, MoO_3, WO_3, V_2O_5, MgO, CdO, TiO_2, GeO_2, ThO_2, Ta_2O_5, La_2O_3). Self-drying during the glass-melting process brought about by the addition of ZnF_2 significantly reduced the intensity of the OH absorption bands at 3.2 and 4.5µm (Stanworth 1952b) [5].

TeO_2-PbO and TeO_2-PbO-SeO_2 glasses (at 578 nm) have refractive indices larger than 2.1, and their thermal expansion coefficients range from 20 to 40 x 106 $^\circ C^{-1}$ between 100 and 200 degrees Celsius (Stanworth 1952b) [5]. The expansion coefficients were measured between 100 and 200 degrees Celsius to arrive at these conclusions. Each of the glasses was found to be very resistant to the dampness common in laboratories. When exposed to an environment with a high concentration of water vapour at temperatures between 50 and 55 degrees Celsius, glasses constructed of BaO, NaO, Li_2O, and B_2O_3 broke with the least resistance. Citric acid and sodium carbonate solution hardly affected any of the glasses. Glasses comprising TeO_2-PbO and TeO_2-BaO-As_2O_5, as well as ternary lead tellurite glasses including P_2O_5, ZnF_2, BaO, Li_2O, and Na_2O, all showed significant alkali attack. Glasses containing d-block oxides, such as MoO_3, WO_3, and Nb_2O_5, have the highest combined resistance to acids, bases, and liquids (Stanworth 1952b) [5]. Zinc tellurite glasses were the focus of research by Redman et al. in 1967 [8]. This study is the next important one from the early days. Knoop testing showed that these glasses had a hardness of around 270, far lower than silica's 970. (540). These glasses were found to have an approximate transmission of 380 nm to 6.6 µm, with OH absorption bands located at 3.35 and 4.5 µm. Additionally, increasing the TeO_2 concentration pushed the electronic absorption edge to longer wavelengths, suggesting that this glass may be useful as a host for the stimulated emission process. It was shown that optical surfaces could withstand exposure to cold water but were destroyed by hot water, powerful acids, anddilute alkalis (Redman et al., 1967) [8].

2. STRUCTURE

In this part, we'll review the structural make-up of the four main ingredients in the glasses at the heart of this discussion: One may think of molecules like TeO_2, ZnO, NaO, and ZnF_2 as examples. A-TeO_2, also known as paratellurite, is a tetragonal (P43212) oxynitride. Another name for it is tetraoxytellurite. Highly distorted [TeO_6] units were postulated to make up the network in early theories on tellurite glasses. Comparable to rhombic β-TeO_2 (tellurite, space group Pbca), but with four oxygens instead of two, these units have similar physical properties. Both the α- and β-TeO_2 crystalline forms are seen in Figure 1.

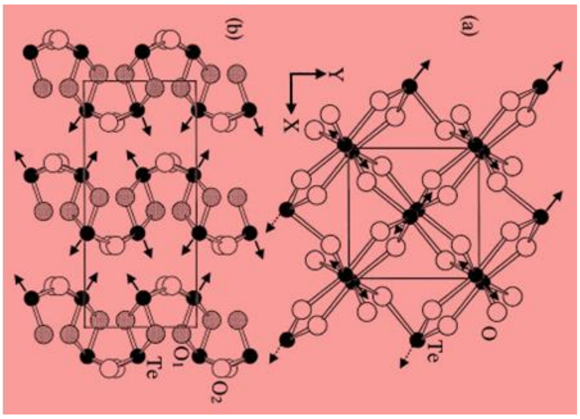
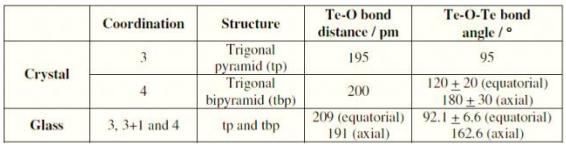


Figure 1:Two different structures of TeO_2 are known: (a) α-TeO2 and (b) α-TeO2. The arrows represent the lone-pair of electrons in Te's 5s shell. (Mirgorodsky et al., 2000) [9]

But new research shows that tellurite crystals and glasses may take on a variety of polyhedral forms with Te^{+4} coordination, including 3, 3+1, and 4. The existence of network modifiers and intermediates in the glasses may account for the observed variation in coordination. Coordination in alpha-TeO_2, beta-TeO_2, and tellurite glasses is summarised in the following **Table 2**.

Table 2: Coordination of both forms of tellurite glasses crystalline TeO2: paratellurite (α-TeO2) and tellurite (β-TeO2).



	Coordination	Structure	Te-O bond distance / pm	Te-O-Te bond angle / °
Crystal	3	Trigonal pyramid (tp)	195	95
	4	Trigonal bipyramid (tbp)	200	120 ± 20 (equatorial) 180 ± 30 (axial)
Glass	3, 3+1 and 4	tp and tbp	209 (equatorial) 191 (axial)	92.1 ± 6.6 (equatorial) 162.6 (axial)

Recent structural studies of tellurite glasses have shown similarities between the network and paratellurite (α-TeO_2), where [TeO_4] units are only linked at their corners. They concluded this after studying the composition and structure of tellurite glasses. Combining TeO_2 with network modifiers like Na_2O and intermediates like ZnO results in the creation of structures that resemble chains. There is a higher chance of glass formation during melt cooling when tellurite minerals like zinc tellurite ($Zn_2Te_3O_8$) are present. Tellurite glasses are known to have corner similarities, yet this fact alone cannot be used to conclude that their fabrication is simple. Pauling's third rule (Tareen and Kutty, 2001) [10] asserts that the stability of ionic tetrahedra (that is, the strength of ionic bonds) declines in a sequence from corner-sharing to edge-sharing to face-sharing. As Pauling's third rule states, by bringing cations in this series closer together, one may strengthen the covalent bond between them (Tareen and Kutty, 2001) [10]. When more tetrahedra share corners than edges or faces, the ionic contact between them increases, and the resulting melts tend to be more viscous. Fast cooling may limit crystallisation because a quick increase in viscosity impedes atomic rearrangement, a necessary step in the crystallisation process. Crystalline and glassy samples of ϒ- and δ-TeO_2 were detected in recent studies by Champarnaud-Mesjard and coworkers, 2000. Heat was applied to binary TeO_2 glasses containing WO_3, Nb_2O_5, or PbO to create ϒ-TeO_2 (5-10 mol. percent). The temperature inside the glasses was maintained at 440 degrees Celsius for the duration of the 60-hour study. X-ray diffraction analysis confirmed beyond a doubt that this phase had an orthorhombic crystal structure with a $P2_12_12_1$ space group. The Raman spectra of these glasses showed a band at 430 cm1 that was consistent with a structural unit comparable to ϒ-TeO_2 (Champarnaud-Mesjard et al., 2000) [11]. These spectacles had this distinctive band. Researchers have proposed the existence of a third phase of δ-TeO_2 called "antiglass", which they believe to represent a transitional state between the crystalline and glassy forms of the material. TeO_2-WO_3 compositions were annealed at temperatures between 5 and 10 mol to create this phase. X-ray diffraction analysis confirmed that δ-TeO2 has a fluorite-like structure that is metastable and has the space group Fm3m, similar to that of fluorite.

2.1 TeO_2-ZnO

Zinc oxide, like wurtzite, has a hexagonal crystal structure and the space group P63mc (ZnS). Oxygen anions occupy the alternating tetrahedral gaps between zinc cations in a hexagonally tightly packed (hcp) arrangement (Tareen andKutty., 2001) [10]. Zinc and oxygen may be understood as interpenetrating hcp sublattices in this structure since they both occupy the same four-coordination sphere.

Kozhukharov et al 1986[11] used neutron diffraction to determine the structure of a glass containing 80 mol of TeO_2 and 20 mol of ZnO. $Zn_2Te_3O_8$ and α-TeO_2 share structural units with glass, although $Zn_2Te_3O_8$ is more common. The structural units in glass are similar to those in zinc oxide. Research indicates that tellurium normally has a coordination number of 3.35, which is in line with current expectations. Glass made from crystalline α-TeO_2 and zinc tellurite with unchanged interatomic distances (Te-O and Zn-O). In the lack of central symmetry in [TeO4], one of the axial bonds (Te-O_{ax}) may stretch with addition of a second component, leading to the production of [TeO_{3+1}]. In other cases, such as in the complex $K_2TeO_3.3H_2O$, the Te-O bonds are significantly lengthened, necessitating a different notation for the structural unit: [TeO_3]. The typical duration of such partnerships is between 1.85 and 3.87 years. Glassy zinc tellurite was found to be 35% [TeO_4], with the remaining 65% being [TeO_3] / [TeO_{3+1}].

Weak cation linkages (Te-Te and Te-Zn through oxygen atoms) between chains in the glass were attributed to the emergence of peaks in the neutron diffraction spectrum that are larger than 3 angstroms. The nature of these connections was determined to be Te-Te and Te-Zn. The insertion of [ZnO_{4+1+1}] polyhedra between the chains prevented the preservation of the interchain distances during the production of glass from crystalline materials (Kozhukharov et al 1986) [11]. These zinc structural units may either join the α-TeO_2-like chains when inserted into the channel between chains, terminate chains, or link onto the sides of chains when positioned in the channel. When terminating chains, they might also attach to the side of the link.

Tellurite glass incorporates ZnO in a network as [ZnO_5] and [ZnO6] units, which are structurally distinct from ZnO's crystalline form. The coordination in TeO_2-ZnO glasses is more similar to that in orthorhombic $ZnTeO_3$ and monoclinic $Zn_2Te_3O_8$ crystals than it is to that in ZnO (Shimizugawa et al., 1997) [12]. When there is 21% ZnO present and the temperature reaches 590 degrees Celsius, the TeO_2-ZnO mixture eutectically combines.

The EXAFS investigation was conducted by Smimizugawa et al. 1997 to better understand the composition of various TeO2-ZnO glasses. a-TeO_2 is constructed from distorted octahedra of the compound TeO_6, rather than the regular tetrahedra utilised in glass production. To rephrase, we may argue that pure TeO_2 cannot form glasses because its 6-coordination with the two remaining weak Te-O atoms inhibits the creation of a tetrahedral amorphous structure. By Zachariasen's definition, Te^{+4} is a network former since the existence of a second piece lowers the critical number to either 3 or 4. It has been shown that the presence of ZnO causes a transition in the structural units from [TeO_4] tbp to [TeO_3] tp through [TeO_{3+1}] polyhedra. Figure 2 displays this variation (2.3).

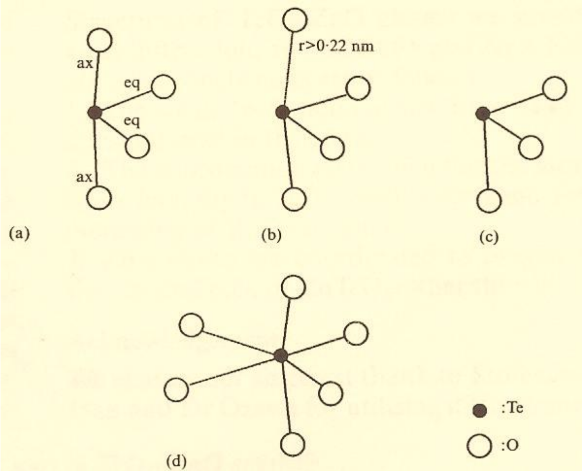


Figure 2:TeO2-ZnO glass structural units in: (a) [TeO4] tbp, (b) [TeO3+1]polyhedra,(c) [TeO3] tp, and (d) [TeO6] in α-TeO2(Shimizugawa et al., 1997) [12]

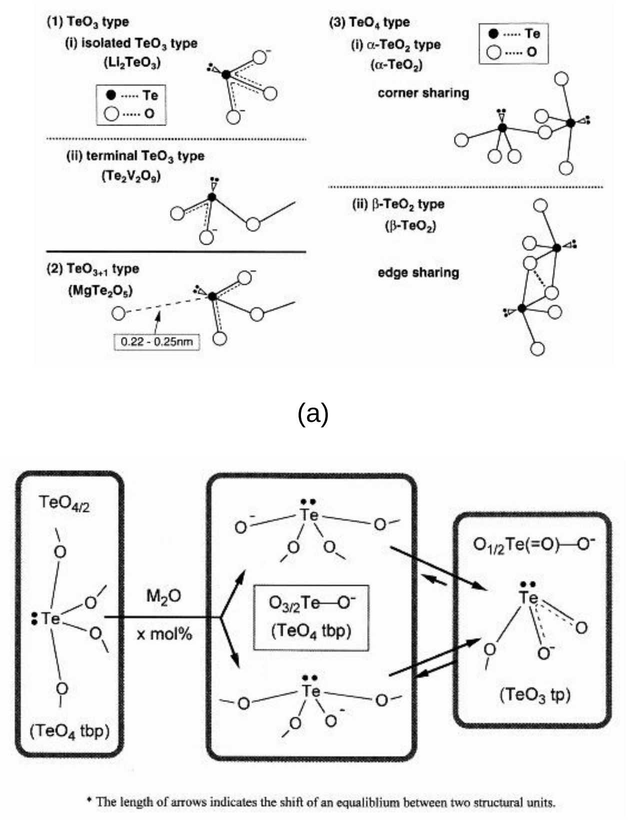
In contrast to the tetrahedral [ZnO4] structure observed in ZnO(Shimizugawa et al., 1957) [12], the zinc atoms in glasses are occupied in the [ZnO_6] and [ZnO_5] structures, like those seen in $Zn_2Te_3O_8$ and ZnTe3, respectively.

2.2 TeO_2-Na_2O.

Sodium's monovalent nature implies it dissociates from oxygen-based bonds in networks. Depolymerization of TeO_2 glasses will occur to a far greater extent with addition of Na_2O, a network modifier, than upon addition of ZnO. Utilizing X-ray photoelectron spectroscopy, Himei et al. 1997[13] studied the make-up and structure of alkali (Li, Na, K, Rb, and Cs) tellurite glasses (XPS). Valence band spectra changed from having the [TeO_4] tbp structure to having the [TeO_3] tp structure upon the introduction of alkalis (from 0 to 30 eV). The [TeO_4] tbp contains a single electron pair. The [TeO_3] sp^3 hybrid orbital and the tellurium sp3d hybrid orbital both have electrons in their equatorial regions.

Zwanziger et al. 1997 used spinecho nuclear magnetic resonance to study the sodium distribution in TeO_2-Na_2O glasses [14]. Twenty mole percent Na_2O has been demonstrated to be the sweet spot for stability. Sodium was found to be located at different positions in the glass than it is in crystalline $Na_2Te_4O_9$, and the spacing between sodium atoms in the glass was found to be much shorter than what would be expected from a uniform distribution centering on 20 mol percent of the element. This structural difference at optimal glass stability may provide a high enough energy barrier to halt structural rearrangement and, by extension, crytallization.

To learn more about the composition and structure of alkali-metal tellurite (Li, Na, K, Rb, and Cs) glasses, Sakida et al. 1999 used nuclear magnetic resonance [15]. The various structural units of the glasses and the possible entrance locations for M_2O into the glass network are shown in Figure 3.



(a)

(b)

Figure 3: What makes glasses interesting is (a) the wide range of structural units seen, and (b) the mechanisms by which M_2O was incorporated into the glass network (Sakida et al. 1999) [15].

It was shown that the composition of the glass altered when alkali was added; the non-bridging oxygens (NBOs) in the [TeO_4] units were replaced by NBOs in the [TeO_3] units (Sakida et al. 1999). This was shown by the increased abundance of [TeO_4] and [TeO_3] units with NBOs in the glass.

McLaughlin et al. conducted experiments with neutron diffraction, X-ray diffraction, and nuclear magnetic resonance to confirm that TeO_2-Na_2O glasses contain all five polyhedra depicted in Figure 4.

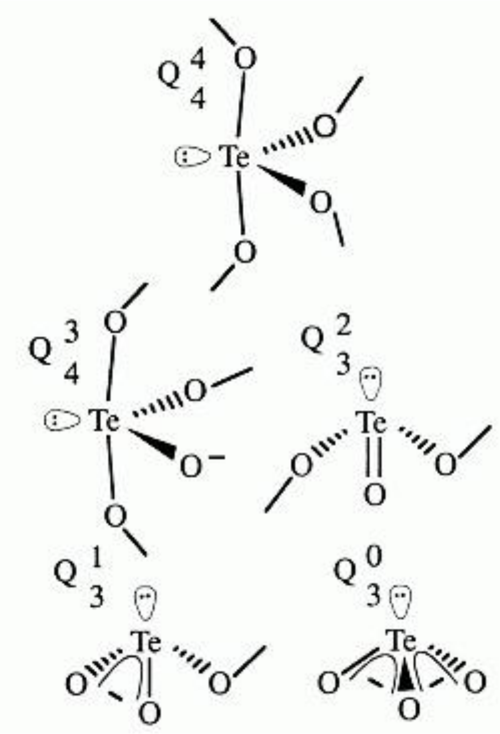


Figure 4: TeO_2-Na_2O glasses often display a variety of polyhedra, represented by the symbol nm Q for the structural unit Q. A central tellurium atom is linked to m oxygen atoms through bridges made from n oxygen atoms (McLaughlin et al., 2000). [16]

When Na_2O is present, the TeO_2 network is constantly cleaved (McLaughlin et al., 2000) [16], leading to an equilibrium population and type of polyhedra that are compositionally dependent. It has been revealed that crystalline sodium tellurites include dimers linked together by four-member rings. However, in TeO_2-Na_2O glasses, only a small percentage of the tellurium atoms adopt a ring shape (around 3 percent). This finding may explain why glasses are so tough to break and hints that devitrification requires a major structural reorganisation. There was also found to be a high concentration of sodium cations close to the eutectic composition, which included 20 mole percent of Na_2O (From) towards the Glass. ((McLaughlin et al., 2001) [17]

2.3 TeO_2-ZnF_2.

Tetragonal ZnF_2 (space group $P4_2/mnm$) has a structure comparable to rutile (TiO_2). Zinc cations are organised such that they are surrounded by fluorine anions at octahedral sites. Since each fluorine ion is surrounded by three zinc ions, there are a total of six zinc ions around each zinc ion. This points to the incorporation of [ZnF_6] units into the tellurite glass matrix, and it is possible that the sequence [$ZnF_{6-x}O_x$], where x might be 1, 2, 3, 4, 5, or 6, has many structural units. Zinc may coordinate six times with both F^- and O^{-2} anions, allowing for this substitution to occur. This is due to the similar ionic radii of F^- and O^{-2}. Reducing the amount of ZnO in tellurite glasses by adding ZnF_2 may provide a composition with stability on par with or even better than pure oxide compositions. Raman spectra of a ternary glass system (TeO_2-ZnO-ZnF_2) were investigated by Sidebottom et al. 1997 [18], who discovered some intriguing findings. However, the Raman bands at 650-750 cm^{-1}, which result from the symmetric stretching modes of TeO_2 structural units ([TeO_4], [TeO_{3+1}], and [TeO_3]), were unaffected by the incorporation of fluoride. The relevant structural units were [TeO_4], [TeO_{3+1}], and [Te_3]. As ZnF_2 concentration increased, however, the bending mode strength at 420 cm-1 increased. The results indicated that fluorine could easily substitute for oxygen in the glassy network without triggering further depolymerization. The strength of the bending mode at 420 cm^{-1} rises with increasing fluoride concentration in this glass because more [TeO_3] units are converted to [$Te(O,F)_{3+1}$]. Although it was shown that ZnO would lead to depolymerization when added does not provide the same results as Na2O. To put it another way, it just wouldn't have the same effect [18].

3. CONCLUSION

Studies of tellurite base glass have been done. By adding modifiers as ZnO, ZnF_2 and Na2O structure of the system get changed and hence properties.

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