IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 415115 (9pp) doi:10.1088/0953-8984/19/41/415115

Structure of $Ag_xNa_{1-x}PO_3$ glasses by neutron diffraction and reverse Monte Carlo modelling

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Received 1 May 2007, in final form 25 June 2007
Published 27 September 2007
Online at stacks.iop.org/JPhysCM/19/415115

Abstract

We have performed structural studies of mixed mobile ion phosphate glasses $Ag_xNa_{1-x}PO_3$ using diffraction experiments and reverse Monte Carlo simulations. This glass system is particularly interesting as a model system for investigations of the mixed mobile ion effect, due to its anomalously low magnitude in the system. As for previously studied mixed alkali phosphate glasses, with a much more pronounced mixed mobile ion effect, we find no substantial structural alterations of the phosphorous–oxygen network and the local coordination of the mobile cations. Furthermore, the mobile Ag^+ and Na^+ ions are randomly mixed with no detectable preference for either similar or dissimilar pairs of cations. However, in contrast to mixed mobile ion systems with a very pronounced mixed mobile ion effect, the two types of mobile ions have, in this case, very similar local environments. For all the studied glass compositions the average Ag–O and Na–O distances in the first coordination shell are determined to be 2.5 ± 0.1 and 2.5 ± 0.1 Å, and the corresponding average coordination numbers are approximately 3.2 and 3.7, respectively. The similar local coordinations of the two types of mobile ions suggests that the energy mismatch for a Na^+ ion to occupy a site that previously has been occupied by a Ag^+ ion (and vice versa) is low, and that this low energy mismatch is responsible for the anomalously weak mixed mobile ion effect.

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

1. Introduction

One of the challenges that has to be faced in order to fully understand ion conduction in glassy electrolytes is the mixed mobile ion effect (MMIE). The MMIE (also called the mixed alkali effect, since the effect is usually largest for alkali glasses) is observed as a drastic decrease in

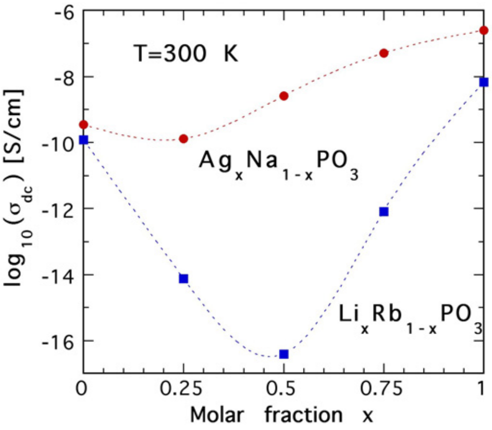

Figure 1. DC conductivity measurements at room temperature of $Ag_xNa_{1-x}PO_3$ and $Li_xRb_{1-x}PO_3$ glasses ($x = 0, 0.25, 0.5, 0.75, 1$), showing the anomalously weak MMIE in the Ag/Na system (one order of magnitude) compared to the Li/Rb glass with its six orders of magnitude drop in conductivity.

properties related to ionic transport, such as ionic conductivity, when one type of mobile ion is partially replaced by another type of mobile ion [1, 2]. In, for instance, the $Li_xRb_{1-x}PO_3$ glass system the conductivity at an intermediate composition is about eight orders of magnitude lower than that of the single alkali glasses [3]. Properties related to structural relaxation, such as viscosity and glass transition temperature, may also exhibit some deviations from linear behaviour, although similar deviations from linearity are observed also for mixed glass-forming systems, which do not contain any mobile cations. Other macroscopic properties such as molar volume and density, refractive index, thermal expansion coefficient and elastic moduli usually change linearly or only slowly with composition [1, 2]. One should also note that the MMIE is not unique for glassy ion conductors but is also present in crystalline compounds, such as (Na, K)-β-Al_2O_3 [4].

Experimental studies have also shown that the MMIE tends to increase with increasing size difference between the mobile ions and that the effect decreases with increasing temperature or frequency of the experiment. These experimental observations in combination with results from molecular dynamics (MD) simulations [5, 6] and *ab initio* molecular orbital calculations [7] suggest that the magnitude of the MMIE is strongly related to the energy mismatch for ionic jumps to dissimilar sites. This implies that in the present study, where the structure of the glass system $Ag_xNa_{1-x}PO_3$ has been investigated, a relatively weak MMIE can be expected due to the similar ionic radii of Ag^+ and Na^+ ions. Indeed, this is also what has been observed from our recent conductivity measurements, which have shown that the drop in conductivity compared to a linear behaviour is only one order of magnitude at 300 K; see figure 1. A comparison to the conductivity data of our previously studied glass system $Li_xRb_{1-x}PO_3$ [3, 8–10], which exhibits an exceptionally strong MMIE as shown in figure 1, shows that the MMIE is anomalously weak for the $Ag_xNa_{1-x}PO_3$ glass system. Detailed experimental and computational comparisons of these two glass systems are therefore highly interesting for reaching a general understanding of the MMIE in glasses.

In recent years the understanding of the MMIE has been considerably improved. The progress has mainly arisen from MD simulations [5, 6, 11] and other computational methods [10, 12] that have allowed studies of the migration pathways and the conduction mechanism in more detail than experimentally possible. However, both these computational studies as well as other experimental investigations have mainly been focused on glass systems with relatively strong MMIE (about five orders of magnitude or more at room temperature), where jumps to dissimilar sites are so energetically unfavourable that they almost never occur. Thus, in ‘strong’ MMIE systems the two types of mobile ions have, to a good approximation, distinctly different conduction pathways [10]. However, such a model for the ionic conduction probably does not apply to the anomalously weak MMIE in the $Ag_xNa_{1-x}PO_3$ glass system. This implies that in this case the conduction process must be different in some way, and therefore an understanding of the conduction process in this system is of particular interest.

In this paper we focus on the microscopic structure of the glasses. From previous findings in the literature it has been established that a metal oxide added to the P_2O_5 glass works as a network modifier and causes the three-dimensional P–O network to break up into chains of interconnected PO_4 units. Furthermore, ^{31}P nuclear magnetic resonance (NMR) spectroscopy [13] has shown that for the metaphosphate composition each PO_4 tetrahedron shares two of its four vertices with others. Thus, about 2/3 of the oxygens are non-bridging and are likely to be surrounded by cations. Both Raman [14] and far-infrared [14] spectroscopy as well as neutron [15] and x-ray [16, 17] diffraction experiments and extended x-ray absorption fine structure (EXAFS) investigations [18] have also established that different kinds of cations have different local environments. Since this latter issue seems to be of high importance for the MMIE our main aim is to determine the local structure (and structural differences) around the mobile Na^+ and Ag^+ ions. Moreover, we are interested in elucidating possible structural alterations in the mixed cation glasses, and in the distribution and degree of mixing of the two types of mobile ions. The studies are based on neutron diffraction experiments in combination with reverse Monte Carlo (RMC) modelling [19] of the microscopic glass structures.

2. Experimental section

Glass samples of composition $Ag_xNa_{1-x}PO_3$ (with $x = 0, 0.25, 0.5, 0.75$ and 1) were prepared by melt quenching. The single metal salt compositions for the Ag and Na systems were obtained by mixing $(NH_4)_2HPO_4$ and $AgNO_3$ and $(NH_4)_2HPO_4$ and Na_2CO_3 in stoichiometric amounts and allowing them to react in a furnace at 600 and 800 °C respectively. The melt was kept at that temperature for at least 1 h and then poured onto a steel mould and pressed to a thickness of 3 mm. The mixed compositions were then produced by crushing and mixing the appropriate amounts of the single mobile cation glasses, melting them and allowing the melt to equilibrate for 2 h above 700 °C before quenching them as described above. The produced samples where homogeneous and transparent with a yellow tint that deepened in intensity with increasing Ag content. The atomic number densities were 0.073 ± 0.001 Å^{-3} for all the investigated glasses.

The neutron diffraction experiments were performed on the liquid and amorphous materials diffractometer, SANDALS, at the Rutherford Appleton Laboratory, UK. This instrument is optimized for the study of light element-containing liquids and amorphous solids. The glass samples where ground into powders and contained in $Ti_{0.68}Zr_{0.32}$ alloy flat plate sample cells, with internal dimensions of $1 \times 35 \times 35$ mm^3 and a wall thickness of 1.1 mm. The data were collected at 2θ angles of 3.5°–40° with incident neutron wavelengths in the range 0.05–4 Å, giving rise to a total momentum transfer (Q-range) of 0.1–50 Å^{-1}. All measurements were conducted at an ambient instrument temperature of about 20 °C. After collection, the data were corrected for contributions from the empty cell and the instrument, absorption, and multiple scattering and normalized to absolute units using a vanadium standard. For each detector bank, only the wavelength region where the silver resonance did not affect the measured intensity was included in the merging of the different detector banks. For these corrections we used the program Gudrun [20], based upon the ATLAS package [21].

As mentioned above, it is well established that the structure of meta-phosphate glasses consists of PO_4 tetrahedra sharing two corners and thus forming polymer-like chains. The alkali ions coordinate to the non-bridging oxygens of the PO_4 chains and provide weaker ionic links between the strongly bonded covalent chains [16]. In order to produce realistic structural models of the glasses, using the RMC modelling method [19], it is important that the models are consistent with the available structural knowledge. To ensure this each phosphorous atom was constrained to be four-fold coordinated by oxygen, $1/3$ of the oxygen atoms coordinated by two phosphorus atoms (bridging oxygens), and $2/3$ of the oxygen singly coordinated (non-bridging oxygens). In this way phosphate chains with two non-bridging oxygens per PO_4 unit were obtained. To further ensure that each mobile cation was realistically coordinated by oxygen (i.e. sensible bonding distances and coordination number) a soft bond-valence constraint was used to minimize the deviation from the expected valence sum of one, as described in [22]. Closest approach distances were also used for all the different atomic pairs, and these were determined from the experimentally obtained pair correlation functions and tabulated ionic radii. When fitting the RMC structural model to experimental data, it proved necessary to reduce the smallest allowed O–O distance to an unphysically low 2.0 Å, in order to achieve a good agreement with the experimental data in the high-Q region of the mixed compositions. This may be due to slight water contamination of the samples. The structure factors calculated from the RMC structures are also slightly higher than the experimental data in the low-Q region for the mixed $x = 0.75$ and 0.5 compositions which may be attributed to an insufficient correction of inelastic scattering. All the five RMC produced models of the glasses contained 4000 atoms, and the size of the simulation boxes was set to satisfy the macroscopic density of the systems.

3. Results and discussion

Figure 2 shows the static neutron structure factors, $S(Q)$ for the five glass compositions in this study, compared to the corresponding structure factors from the RMC produced structural models. The striking similarity between the structure factors of the different composition leads us to directly conclude that there are no major structural differences between either the two single metal ion glasses or between the mixed compositions and the single metal ion compositions. Small changes occur in the low-Q region due to differences in scattering length between Ag and Na. This is effectively shown by viewing the partial structure factors, extracted from the RMC models. In figure 3, these have been plotted for the two single cation compositions, and they reveal a remarkable similarity in the structure of the two glasses. The differences that are present are difficult to separate from experimental errors and structural modelling errors. Thus, in these systems where the two mobile ions have nearly the same size, we see no change of the P–O network or overall structure due to a change of oxide. The $S(Q)$ of the 25% Ag composition exhibits a broader peak at 5.5 Å^{-1} which is also shifted towards a slightly lower Q with respect to the other compositions. This may be due to a partial phase separation of metal ions forming small amounts of metallic Ag/Na, and a sub-meta composition of the remaining glassy phase.

The mobility of cations in glasses is strongly dependent on their local environment. Figure 4 shows the partial pair correlation function $g_{\mathrm{M-O}}(r)$ for Ag and Na, extracted from the RMC structure models. From the similarities of the oxygen coordinations in single and mixed cation compositions it is evident that the local environment of each ion is insensitive

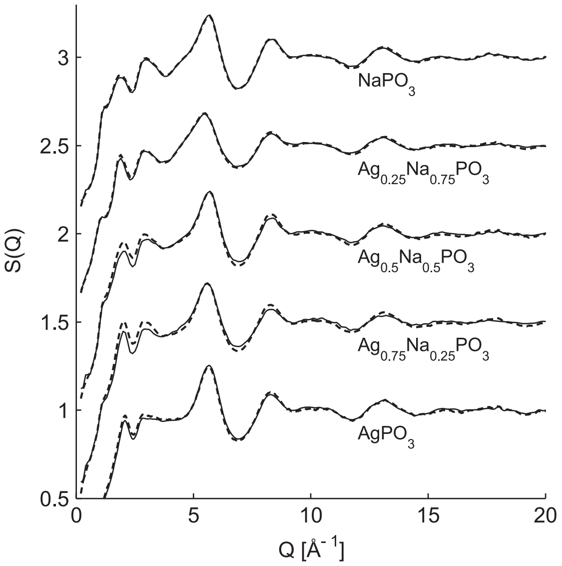

Figure 2. Experimental neutron structure factors (full lines) and computed neutron weighted structure factors for the RMC configurations of mixed and single $Ag_xNa_{1-x}PO_3$ glass. Consecutive curves are shifted by 0.5 units for clarity.

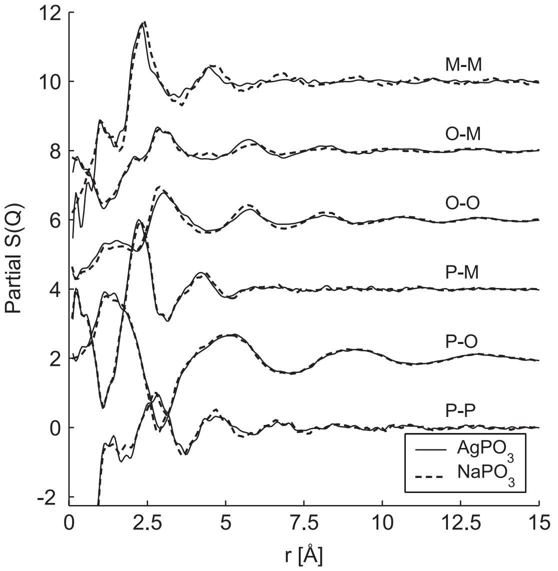

Figure 3. Partial $S(Q)$ for the single cation glasses $AgPO_3$ and $NaPO_3$, obtained by Fourier transform of the corresponding atomic pair correlations in the RMC produced structural models, showing the similarities in structure. Consecutive curves have been shifted by two units for clarity.

(within the experimental errors) to the presence of another type of mobile ion in the glass. In table 1, the average M–O bond distances and coordination numbers (integrated up to 2.8 Å) are summarized. It is clear that the average numbers of coordinating oxygens are similar across the glass compositions for both Ag and Na, as well as similar to each other. These results are

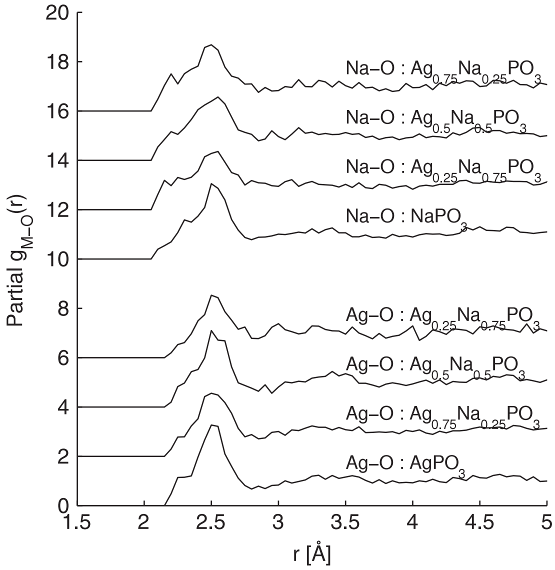

Figure 4. Partial pair correlation functions, $g_{M-O}(r)$, for Ag and Na obtained from the RMC produced structural models of the $Ag_xNa_{1-x}PO_3$ glasses. Consecutive curves are shifted by two units and $g_{Na-O}(r)$ is shifted an additional ten units in the graph. Noise in the curves increases for glasses with low M-ion content due to the low number of atoms in the structural model to average over.

Table 1. Average bond distances (r_{M-O}) and coordination number (N_{M-O}) for the nearest metal ion–oxygen distances extracted from the RMC models. The coordination numbers were obtained by integration over the first peak in the partial $g_{M-O}(r)$ ($r = 2.8$ Å). The differences in coordination numbers are within the experimental error.

Glass	M–O	$\langle r_{M-O}\rangle$	$\langle N_{M-O}\rangle$
$AgPO_3$	Ag–O	2.5 ± 0.1	3.61
$Ag_{0.75}Na_{0.25}PO_3$	Ag–O	2.5 ± 0.1	3.18
	Na–O	2.5 ± 0.2	3.84
$Ag_{0.5}Na_{0.5}PO_3$	Ag–O	2.5 ± 0.1	3.33
	Na–O	2.5 ± 0.1	3.82
$Ag_{0.25}Na_{0.75}PO_3$	Ag–O	2.6 ± 0.2	2.93
	Na–O	2.5 ± 0.1	3.57
$NaPO_3$	Na–O	2.5 ± 0.1	3.59

consistent with a previous study of $A_xB_{1-x}PO_3$ (A, B = Li, Na and Rb) glasses where each ion was found to retain its local environment in all glass compositions [23]. Furthermore, in the present study both types of mobile ions have the same average M–O distance of 2.5 Å in all compositions.

The insensitivity in oxygen coordination with respect to glass composition could be due to a 'micro phase separation' or the formation of clusters of similar cations, thus creating regions in the glass of single-ion-like structure. This tendency for clustering of either like or unlike metal ions may be investigated by calculating the coordination number M_i–M_j as a function of distance from a central cation i. Figure 5 shows such integrated coordination numbers for all glass compositions and all cation pairs, scaled by the relative abundance of cation j.

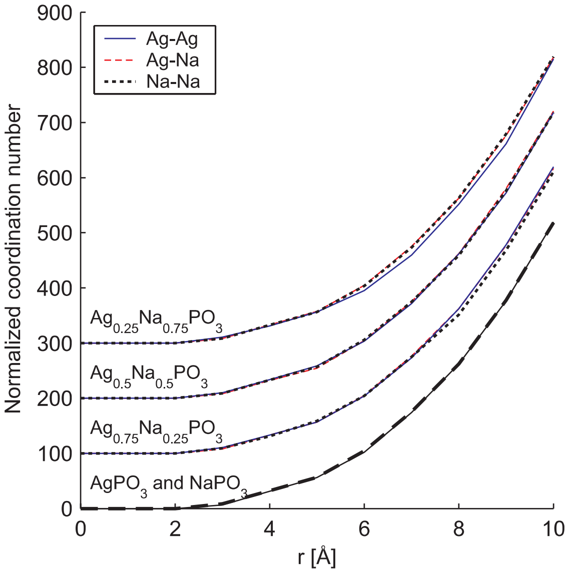

Figure 5. Normalized metal ion–metal ion coordination numbers as a function of distance from a central ion, $N_{ij}(r)$, for the $Ag_xNa_{1-x}PO_3$ glass system. The M_i–M_i correlations of the two single cation glasses are at the bottom ($AgPO_3$, solid line, and $NaPO_3$, dashed line). The M_i–M_i, M_i–M_j coordinations for the mixed mobile ion compositions ($x = 0.25, 0.5, 0.75$) are shifted by 100 units for clarity. The coordination numbers have been scaled by the number density of the coordinating metal ion.

If a tendency for clustering of either similar or dissimilar cations were present in any of the compositions, it would show up as a significant difference between M_i–M_j and M_i–M_i in the coordination numbers integrated up to a given distance (r-value). However, no such tendencies are visible, suggesting that the Ag and Na ions are randomly mixed in the glasses. In the $x = 0.25$ and 0.75 compositions, the M_i–M_i coordination number for the minority ion drops slightly below that of the other coordination numbers at distances above 5 Å. This may be due to inhomogeneities in the distribution of metal ions throughout the structure that becomes more prominent when the number of neighbours of the same type is low.

The structure of the P–O network and the distribution of the mobile ions is most easily envisioned by viewing a slice of the modelled structure. Figure 6 shows a 9 Å thick slice through the RMC model of the $Ag_{0.5}Na_{0.5}PO_3$ glass. The mobile ions can be seen to be distributed along low-dimensional channels, leading through the phosphate network, in agreement with the modified random network model by Greaves [24]. It is also evident that the mobile ions are randomly mixed and distributed throughout these channels without any clustering behaviour. It could be argued that this random mixture is a direct consequence of our limited experimental data, since in this study we have only used neutron diffraction data as input to our structure models. These neutron data are foremost sensitive to correlations involving oxygen. X-ray diffraction studies, where Ag correlations would dominate, would complement the modelling with additional information on the mobile ion distribution. Reliable x-ray data for the mixed compositions are presently not available, but the structural models presented here are likely to only be slightly refined by the addition of x-ray data. Our previous studies of other mixed alkali phosphate glasses with Li, Rb and Na as mobile ions that have combined neutron and x-ray diffraction data have shown that the mobile ions in these glasses are randomly mixed despite the large differences in ionic sizes. Hence, the distribution of Ag

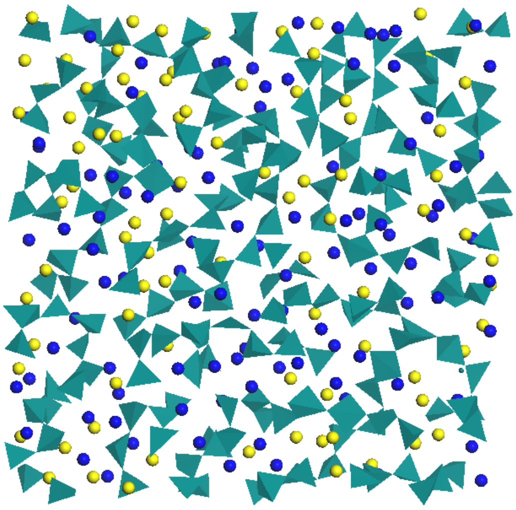

Figure 6. A 9 Å thick slice through the RMC produced model of the $Ag_{0.5}Na_{0.5}PO_3$ glass. PO_4 units are drawn as tetrahedra, Ag as dark grey spheres (blue online) and Na as light grey spheres (yellow).

and Na should therefore also be expected to be a random mixture, in particular since their ionic sizes are very similar.

We have here shown striking similarities in the oxygen coordination of Ag and Na ions in the glass system $Ag_xNa_{x-1}PO_3$. Based on this, we propose that the unusually low mixed mobile ion effect in this glass system stems from these similarities in local environment. Several computational studies [5–7, 11, 12] of mixed mobile ion systems with more prominent MMIE have attributed the decrease in conductivity to the energy penalty for an ion of type A to occupy a site adopted for an ion of type B. The two mobile ions also exhibit distinctly different diffusion pathways and will thus effectively block each other's paths, even in low concentrations of the minority ion due to the low-dimensional structure of the channels in which the ions reside. In the $Ag_xNa_{1-x}PO_3$ phosphate system, where the two mobile ions have very similar local environments, it is reasonable to assume that there is an exceptionally low energy mismatch associated with a jump of an Ag ion to an Na site and vice versa. This small energy mismatch for a jump to a dissimilar site probably allows the ions to move along the same diffusion pathways. The blocking effect of dissimilar ions, discussed in [10, 25], is thus not nearly as effective in the mixed mobile ion glasses studied here, and can thus explain the weak MMIE. A more detailed investigation, based on bond valence analysis [10] of the two types of mobile ions, will be presented in a forthcoming publication.

4. Conclusion

We have here shown that the weak MMIE in a mixed Ag/Na phosphate glass can be attributed to the similar local environments of the two types of mobile ions. They share a similar coordination to oxygen both in coordination number and in average distance to the nearest oxygens. We suggest that this similarity between sites adapted to the different ions allow Ag and Na to share common diffusion pathways, since the jump of an Ag ion to a site adopted for Na, and vice versa, is associated with only a small energy mismatch. This drastically reduces the blocking effect seen in other mixed mobile ion systems, such as $Li_xRb_{1-x}PO_3$ glasses, where the two mobile ions have distinctly different pathways.

Acknowledgments

Financial support from the Hi-Condelec (NMP3-CT-2005-516975) EU STREP project, support to JS from the Swedish Foundation for Strategic Research and to StA from the NUS Academic Research Fund (R284000029112/133) is gratefully acknowledged. JS is a Royal Swedish Academy of Sciences Research Fellow supported by a grant from the Knut and Alice Wallenberg Foundation.

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