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Solid State Ionics 177 (2006) 223 – 228

SOLID STATE IONICS

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Sr and Ga substituted $Ba_2In_2O_5$: Linking ionic conductivity and the potential energy surface

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Received 30 August 2005; received in revised form 24 October 2005; accepted 8 November 2005

Abstract

We study in detail the potential energy surface of Ga and Sr substituted $Ba_2In_2O_5$ by considering the changes in the relative energies of the local structures of $Ba_2In_2O_5$ when replacing 1 / 8th of the indium atoms with gallium or 1 / 8th of the barium atoms with strontium. The calculations are subsequently used to interpret the increase in ionic conductivity of cubic $Ba_2In_2O_5$ when strontium is substituted for barium and the decrease in ionic conductivity when gallium is substituted for indium. The effects of replacing 1 / 8th of the indium atoms with gallium or 1 / 8th of the barium atoms with strontium are significant and affect considerably the relative stability of the different low energy local structures present for $Ba_2In_2O_5$. While a higher density of low energy structures is observed for $Ba_{1.75}Sr_{0.25}In_2O_5$ than for $Ba_2In_2O_5$, the opposite occurs for $Ba_2In_{1.75}Ga_{0.25}O_5$. This observation supports our main hypothesis: a high density of low energy local structures is a prerequisite for high ionic conductivity.

Keywords: Energy landscape; Ionic conductivity; Modelling; $Ba_2In_2O_5$; Sr-substitution; Ga-substitution; DFT

1. Introduction

Theoretical approaches to the link between the structure, energetics and dynamics of disordered materials demand computational techniques that are able to map the low energy portion of the potential energy surface accurately. Treatment of oxides containing vacancies are demanding in particular since the formation of a vacancy in general is associated with a significant relaxation of the polyhedron from which an oxygen atom is removed [1,2]. We have recently developed a computational approach to investigate highly defective oxides [2,3]. We interpret the average structure observed experimentally at any temperature as a time and spatial average of the different local structures, corresponding to local minima on the potential energy surface, which are energetically accessible. We have concentrated on disordered high-temperature phases formed by oxides taking the brownmillerite-type structure at low temperatures. The brownmillerite structure consists of alternating two-dimensional layers of corner-shared InO_4-tetrahedra and corner-shared InO_6-octahedra. At high temperatures the oxygen atoms and vacancies are disordered and a thorough characterization of the energy hypersurface involves consideration of all possible arrangements of the oxygen vacancies in the lattice. Even for a rather small simulationcell the computational challenge is large. The distribution of 20 oxygen atoms over 24 oxygen lattice sites of a $2 \times 2 \times 2$ supercell of $A_2B_2O_5$ gives 10,626 *initial unrelaxed* arrangements. The complexity of the problem can, however, be simplified taking symmetry into account giving a total of 78 *initial unrelaxed* crystallographically non-equivalent arrangements [2]. Although computationally expensive, structural optimization with respect to *all* unit cell dimensions and atomic coordinates of each of these arrangements is feasible using density functional theory, see e.g., our study of $Ba_2In_2O_5$ [3]. The need for full optimizations of the configurations is stressed since large energy changes accompany the structural relaxations and determine not only the magnitude of the energy differences between the different configurations but even the relative order of energies. It follows that at present only rather small cell-sizes are tractable by density functional theory. Nevertheless, the results obtained for a smaller cell size can be used for considering stacking-sequences and connectivity-patterns present only in larger supercells [3].

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doi:10.1016/j.ssi.2005.11.006

Although the total number of local structures even for the rather small simulation cell used in this study is very large, relatively few configurations, associated with different arrangements of BO$_4$-tetrahedra, BO$_5$-square pyramids and BO$_6$-octahedra, are thermally accessible at most temperatures [2,3]. The energies of these different local structural environments must be taken into account when considering mechanisms of ion transport. A conventional vacancy jump mechanism requires different types of local short-range order that may be high in energy in a particular system and thus make a negligible contribution. For example, mechanisms involving square-planar InO$_4$ coordination will be high in energy because of the relatively high energy of this coordination [3]. Studies of transition paths connecting different low-energy local structures furthermore indicate that collective ion movements are energetically significant compared to single-jump mechanisms in fast oxide-ion conductors such as $Ba_2In_2O_5$ [4].

A complete map of the minima on the potential energy surface is often not needed and in general too expensive to be used in routine investigations of disordered systems. Strategies for selecting a priori a representable set of local structures are thus needed for handling complex systems more efficiently. We have recently shown that the low energy portion of the potential energy hypersurface can be mapped at low computational cost using genetic algorithms [5]. Alternatively, efficient mapping can be obtained by dividing the different local structures into groups of configurations according to a radial-distribution function [2]. In other cases chemical similarities between different compounds/systems and e.g., knowledge of polyhedron preference can be used to restrict the search space and the location of only a few local structures (energy minima) may be sufficient for gaining significant information. Such an approach has e.g., recently been used to consider criteria for fast-ion conduction in perovskite related A_2B_2O$_5$ oxides [6]. A high density of low lying energy minima was proposed to be the main prerequisite for high ionic conductivity. It was suggested that the possibility of many different oxygen orderings associated with a variety of low-energy connectivity schemes within the tetrahedral layers of the brownmillerite-based structures of $Sr_2Fe_2O_5$ and $Ba_2In_2O_5$ results in the necessary high density of low lying energy minima, giving rise to many low energy transition pathways for oxygen-ion transport [6].

In the present paper we approach even more complex systems in a search for further evidence for correlations between local structure and ionic conductivity. We will use the calculations for $Ba_2In_2O_5$ as our starting point in an attempt to rationalize the increase in ionic conductivity of cubic $Ba_2In_2O_5$ when Sr is substituted for Ba [7] and the decrease in ionic conductivity when Ga is substituted for In [8]. We have shown earlier that the energies of the different connectivity patterns present in $Ba_2In_2O_5$ are largely influenced by the large Ba atoms [3] and we thus must expect significant effects when Ba is substituted by the smaller Sr. Ga on the other hand substitutes for In and here a main issue is the preference of In and Ga for different possible local structural coordinations.

2. Computational details

In our previous studies we focused either on mixed cation systems [9–11] or on systems containing high concentrations of oxygen vacancies [2–4,6]. Here we are dealing with materials containing both types of disorder. We address this additional complexity by considering explicitly the changes in energy for the low energy local structures of the mother phase (in our case $Ba_2In_2O_5$) when making certain substitutions. Previously for $Ba_2In_2O_5$ we considered all configurations constructed by distributing oxygen sites in a $2\times2\times2$ (36-ion) supercell. Many of the *relaxed* local energy minima were high in energy and only a few local structural entities were shown to contribute significantly to the disordered state at most temperatures. Thus, here we have taken a computationally much cheaper strategy in which we investigate the structural features of Sr and Ga substituted $Ba_2In_2O_5$ considering only the energies of the configurations present in the low-energy portion of the energy landscape of $Ba_2In_2O_5$. This approximation is justified as long as the changes in energy are not too large (<1 eV). We have checked that this condition is fulfilled in the present study by carrying out additional structural optimisations for selected high energy configurations. In order to keep track of the different local structures considered throughout the whole paper, the structures considered for $Ba_2In_2O_5$ (10 all together) are numbered in terms of increasing energy. These numbers are included in Figs. 2–4,6. We start out with the relaxed structures of $Ba_2In_2O_5$. One out of the eight Ba or In-atoms in the $2\times2\times2$ supercell $Ba_2In_2O_5$ is substituted by Sr or Ga, respectively. In addition $Sr_2In_2O_5$ and the hypothetical compound $Ba_2Ga_2O_5$ are examined.

Structural optimizations with respect to *all* unit cell dimensions and atomic coordinates of each arrangement are performed using density functional theory within the Generalized Gradient Approximation (GGA). *No* symmetry constraints were imposed during the optimizations. A sufficiently large basis of projected augmented plane waves was used as implemented in the Vienna ab initio simulation program (VASP) [12,13]. Test calculations to check for convergence with increasing energy cut-off and the k-point mesh were carried out. The optimizations are accompanied by large structural changes and a large, constant energy cut-off of 700 eV was used. A 222 k-point mesh was sufficient.

3. Results and discussion

The effects of substituting 1 out of 8 indium atoms in the $Ba_2In_2O_5$ supercell with gallium or 1 out of 8 barium atoms with strontium are significant in that the substitutions affect considerably the relative stability of the different low energy local structures obtained for $Ba_2In_2O_5$ [3]. We stress that we are using only a selection of the low energy local structures of the mother compound $Ba_2In_2O_5$. We believe this approach to be reasonable for representing the low energy portion of the energy surface of the substituted systems, but it is more questionable for $Sr_2In_2O_5$ and in particular for $Ba_2Ga_2O_5$ that does not take a perovskite-related structure. In this context we note that our calculations do reproduce the observed ground state for $Sr_2In_2O_5$. $Ba_2Ga_2O_5$ is unstable with respect to BaO and $BaGa_2O_4$ and thus we can here consider only hypothetical structures; there are no experimental data for comparison.

In order to discuss the changes in the topography of the potential energy surface when making substitutions we need initially to consider the low energy portion of the potential energy surface of $Ba_2In_2O_5$ [3] in some detail. Presentation of the new results for $Ba_2In_{1.75}Ga_{0.25}O_5$, $Ba_2Ga_2O_5$, $Ba_{1.75}Sr_{0.25}In_2O_5$ and $Sr_2In_2O_5$ follows.

3.1. Low energy structures for $Ba_2In_2O_5$

$Ba_2In_2O_5$ adopts the brownmillerite-type structure that consists of alternating two-dimensional layers of corner-shared InO_4-tetrahedra and corner-shared InO_6-octahedra. The room temperature structure of $Ba_2In_2O_5$ was initially described as an ideal brownmillerite-type structure where the InO_4 tetrahedra were assumed to be regularly ordered [14] with empty oxygen-sites, vacancies, arranged in parallel chains as shown in Fig. 1a. For clarity, the Ba-cations are not shown in the figure. There are three crystallographically distinct oxygen sites; O(1) in the equatorial plane of the octahedra, O(2) at the apical sites of the octahedra and O(3) those oxygens in the tetrahedra not shared with the octahedra. Two recent in situ neutron diffraction studies [15,16] indicate that the structure is more complex in that some degree of disorder is present already at room temperature in that the InO_4 tetrahedra centred at the 8*i* position of space group *Icmm* may take two different orientations. The orientation of a given tetrahedron is unlikely to be random and the presence of domains in which all tetrahedra take just one of the two orientations has been suggested [15].

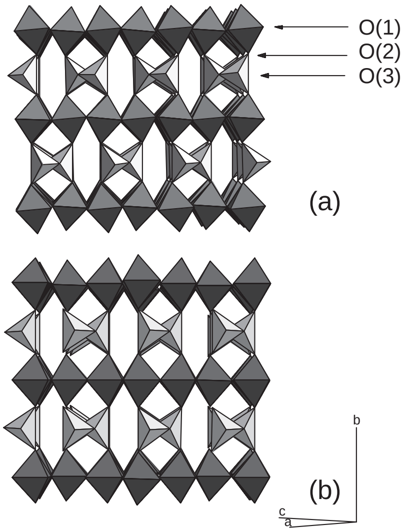


Fig. 1. Polyhedral representation of the two lowest-energy brownmillerite-related configurations. The three different oxygen sites are marked. The two configurations differ in *stacking* of the tetrahedral layers. (a) The experimentally observed stacking where the vacancy channels are staggered along the *b*-axis. (b) The ground state configuration for our model system where the vacancy channels are not staggered.

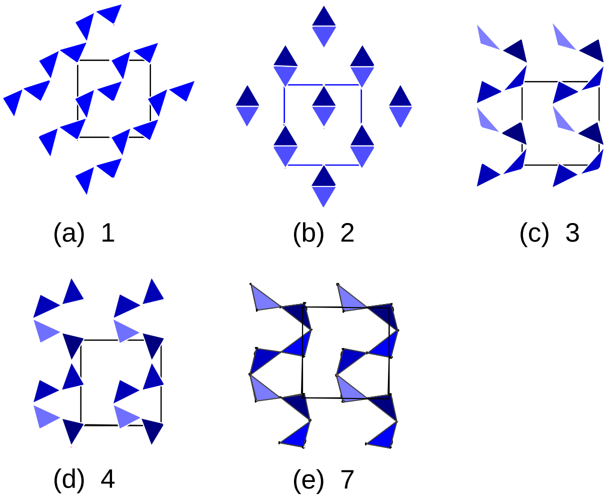
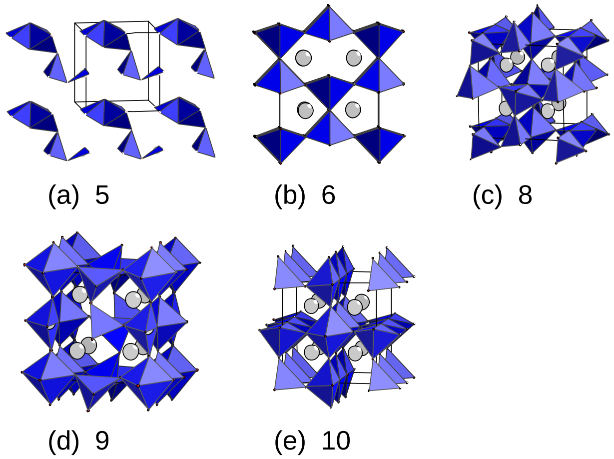


Fig. 2. Connectivity of BO_4-tetrahedra (B = In and/or Ga) in the *ac*-plane of the brownmillerite-related local structures. The numbering refers to the energies for the different local structures of $Ba_2In_2O_5$; the 10 lowest energy configurations are given numbers in order of increasing (less negative) energy.

Our choice of supercell ($2 \times 2 \times 2$) does not permit the formation of the stacking of tetrahedral layers observed experimentally in the ordered low temperature form. The energy of this structure is instead calculated using an orthorhombic 18-atom cell [3]. The lowest energy minimum of our $2 \times 2 \times 2$ supercell differs in the *stacking* of the tetrahedral layers. While the experimentally observed stacking along the *b*-axis in which the vacancy channels are staggered along this axis is present for the real ground state (calculated using the 18-atom cell), the vacancy channels are not staggered in the ground state of the $2 \times 2 \times 2$ supercell. This closely related structure is shown in Fig. 1b.

Five out of the ten low energy configurations considered are relatives of the brownmillerite-type structure in that they consist of alternating layers of InO_4-tetrahedra and InO_6-octahedra. They differ in the type of *connectivity* within the tetrahedral layers as shown in Fig. 2 in order of increasing energy (the numbers also included refer to the numbering introduced above and should be used to identify these structures in Figs. 4 and 6). Fig. 2a show the connectivity observed experimentally and also obtained theoretically for the two lowest-energy configurations (represented by Fig. 1a and b). With increasing energy, configurations characterized by edge-sharing tetrahedra (Fig. 2b), and by zig-zag patterns of tetrahedra (Fig. 2c, d and e) are obtained.

In addition, five low-energy configurations that contain square pyramidal entities are considered. Fig. 3 show these in order of increasing energy (again the numbers included refer to the numbering introduced above and should be used to identify these structures in Figs. 4 and 6). In one of these, one oxygen atom is removed from each InO_6-octahedra yielding a structure built by corner-sharing square pyramids only, see Fig. 3b. This structure resembles the ordered structure adopted by related compounds containing a Jahn–


(a) 5 (b) 6 (c) 8

(d) 9 (e) 10

Fig. 3. Low-energy local structures of $Ba_2In_2O_5$ containing square pyramids. The numbering refers to the energies for the different local structures of $Ba_2In_2O_5$; the 10 lowest energy configurations are given numbers in order of increasing (less negative) energy.

Teller ion such as $Sr_2Mn_2O_5$ [17] and $Ca_2Mn_2O_5$(srebrodolskite) [18].

3.2. Effect of Ga substitution: $Ba_2In_{1.75}Ga_{0.25}O_5$ and $Ba_2Ga_2O_5$

The main effects of substituting In in $Ba_2In_2O_5$ by Ga can be deduced from the energies of the various structures given in Fig. 4. The solid lines in the figure are included to make it easier to follow the changes in the relative energies from $Ba_2In_2O_5$ via $Ba_2In_{1.75}Ga_{0.25}O_5$ to $Ba_2Ga_2O_5$. Dashed lines represent local structures that are unstable and thus relax into a different local environment. A combination of the number-code explained above and a symbol code is used for identifying the different local structures (the energies of the structures given in Figs. 2 and 3 can thus be identified). The black stars for $Ba_2In_2O_5$ represent brownmillerite-related structures that consist of alternating layers of InO_4-tetrahedra and InO_6-octahedra. When replacing one out of the eight indium atoms in the supercell with gallium, the gallium can either be placed in the tetrahedral layer or in the octahedral layer. For $Ba_2In_{1.75}Ga_{0.25}O_5$ the brownmillerite-related configurations with Ga in the tetrahedral layer are given by black stars, while those with Ga in the octahedral layer are given by black triangles. The filled black circles represent configuration 6 containing InO_5-square pyramids only (the structure taken, e.g., by $Ca_2Mn_2O_5$ and $Sr_2Mn_2O_5$), while the open black circles represent the remaining configurations shown in Fig. 3.

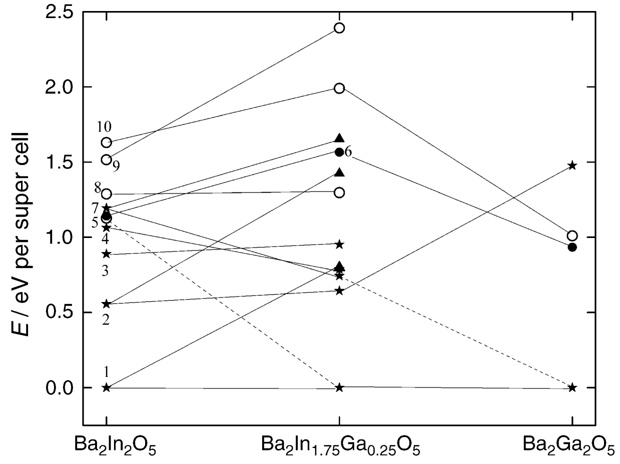


Fig. 4. The $Ba_2In_2O_5$–$Ba_2Ga_2O_5$ system: Energies of the 10 different local structures considered relative to that of the lowest for each compound/composition. The solid lines in the figure are included to make it easier to follow the changes in the relative energies from $Ba_2In_2O_5$ via $Ba_2In_{1.75}Ga_{0.25}O_5$ to $Ba_2Ga_2O_5$. Dashed lines represent local structures that are unstable and relax into a different local environment. The numbering refers to the energies for the different local structures of $Ba_2In_2O_5$; the 10 lowest energy configurations are given numbers in order of increasing (less negative) energy.

Nine out of the ten local $Ba_2In_2O_5$-structures considered are stable also for $Ba_2In_{1.75}Ga_{0.25}O_5$. All except two are higher in energy relative to the ground state compared to $Ba_2In_2O_5$. Gallium shows a much stronger preference for the tetrahedral environment than indium does. Placing the Ga atom in the octahedral layer increases the energy by about 0.8 eV per formula unit compared to locating it in the tetrahedral layer. It should also be noted that one configuration (number 5 see Fig. 3a) is unstable for $Ba_2In_{1.75}Ga_{0.25}O_5$ and relaxes into the chain-type connectivity given in Fig. 1a.

Many of the local structures present in $Ba_2In_2O_5$ and $Ba_2In_{1.75}Ga_{0.25}O_5$ are not stable for $Ba_2Ga_2O_5$. The results for $Ba_2Ga_2O_5$ confirm that gallium shows a high preference for the tetrahedral environment. It is important to note that compounds with composition $Ba_2Ga_2O_5$ have not been reported in literature; compounds with this composition are unstable relative to a two-phase mixture of BaO and $BaGa_2O_4$ [19]. Three perovskite-related structures are obtained and represented in Fig. 4; however other structures are lower in energy. The ground state structure is quite different from the starting point. In the relaxed calculated ground state not all O-atoms are shared between two entities, see Fig. 5, and the structure is not related to the perovskite-type structure and thus not included in Fig. 4 (where the energies are relatively to the lowest perovskite-related configuration). The presence of a zig-zag pattern of corner shared tetrahedra is interesting since a similar zig-zag pattern is obtained also for the lowest energy brownmillerite/perovskite-like configuration. The brownmillerite configuration in which the tetrahedra share edges is also stable for $Ba_2Ga_2O_5$, while the chain-patterned and two of the zig-zag patterned configurations stable for $Ba_2Ga_2O_5$ and $Ba_2In_{1.75}Ga_{0.25}O_5$ are unstable for $Ba_2Ga_2O_5$. Since, the

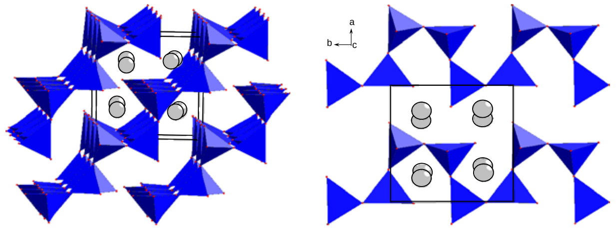


Fig. 5. The ground state structure obtained for a hypothetical compound with composition $Ba_2Ga_2O_5$ (NB: note that $Ba_2Ga_2O_5$ is unstable relative to BaO and $BaGa_2O_4$).

density of low energy configurations is important for ionic conductivity [3,6], this destabilization of some of the possible connectivity patterns is important.

3.3. Effect of Sr substitution: $Ba_{1.75}Sr_{0.25}In_2O_5$ and $Sr_2In_2O_5$

The main effects of substituting Ba in $Ba_2In_2O_5$ by Sr can be deduced from the energies of the various structures (local minima) given in Fig. 6. The solid lines in the figure are included to make it easier to follow the changes in the relative energies from $Ba_2In_2O_5$ via $Ba_{1.75}Sr_{0.25}In_2O_5$ to $Sr_2In_2O_5$. Dashed lines represent local structures that are unstable and thus relax into a different local environment. As in Fig. 4, a combination of a number-code and a symbol code is used for identifying the different local structures. All local $Ba_2In_2O_5$-structures considered are stable also for $Ba_{1.75}Sr_{0.25}In_2O_5$. In contrast to what was observed for $Ba_2In_{1.75}Ga_{0.25}O_5$ versus $Ba_2In_2O_5$, most configurations have lower energy relative to the ground state for $Ba_{1.75}Sr_{0.25}In_2O_5$ than for $Ba_2In_2O_5$. Here it must be emphasized that the ground state changes. While the chain-like connectivity of the brownmillerite structure in agreement with experiment is the ground state for $Ba_2In_2O_5$ [14] and $Sr_2In_2O_5$ [20], it is destabilized in the mixed cation system. The browmillerite-related configuration with edge-sharing tetrahedra is the ground state for $Ba_{1.75}Sr_{0.25}In_2O_5$. We have been unable to find any reports for this composition in the literature and thus this constitutes a prediction to be tested.

We have shown earlier that the relative energies of the different possible connectivity patterns of In–O polyhedra are largely influenced by the large A-site cations and thus by the Ba–O interactions in $Ba_2In_2O_5$ [3]. These interactions are characterized using bond valence sums [21] that correlate well with the relative energy within groups of related configurations [3]. Also, in our present case the changes in the ground state are supported by bond–valence sum calculations. While the average Ba–O bond valence sum for the edge sharing configuration (Fig. 2b) for $Ba_{1.75}Sr_{0.25}In_2O_5$ is 1.85, the value for the chain-like configuration (Fig. 2a) is significantly lower, 1.68. If we compare $Ba_2In_2O_5$ and $Sr_2In_2O_5$ the chain like configuration has higher bond valence sums (1.95 and 1.87, respectively) than the edge-sharing configuration (1.85 and 1.68, respectively). In this picture, rather than a stabilization of the edge-sharing configuration, what we observe is a destabilization of the chain-like configuration. The substitution of 1/8th of the 8 barium atoms in the chain-like local structure (in the 2 × 2 × 2 supercell) with strontium displaces the neighbouring barium atoms away from their oxygen neighbours giving, overall, longer Ba–O interatomic distances and thus a lower bond valence sum.

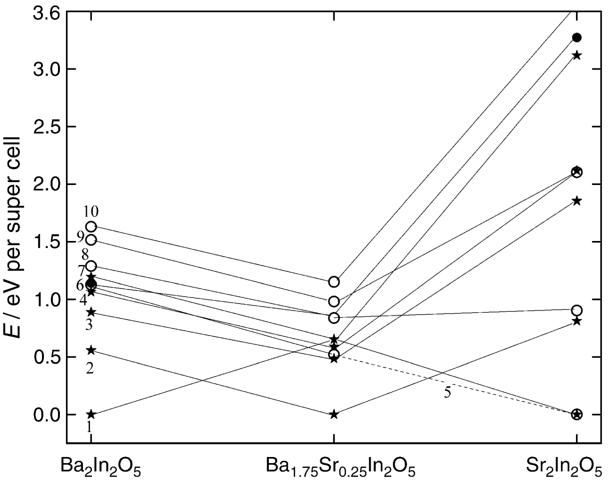


Fig. 6. The $Ba_2In_2O_5$–$Sr_2In_2O_5$system: Energies of the 10 different local structures considered relative to that of the lowest for each compound/composition. The solid lines in the figure are included to make it easier to follow the changes in the relative energies from $Ba_2In_2O_5$ via $Ba_{1.75}Sr_{0.25}In_2O_5$ to $Sr_2In_2O_5$. Dashed lines represent local structures that are unstable and relax into a different local environment. The numbering refers to the energies for the different local structures of $Ba_2In_2O_5$; the 10 lowest energy configurations are given numbers in order of increasing (less negative) energy.

4. Topography of the energy surface and criteria for ionic conductivity

The molar volume of compounds containing tetrahedra are rather large compared to compounds with the same stoichiometry that contain square planar or square pyramidal structural entitites [6]. Thus structures in which tetrahedra are energetically preferred are relatively open. This observation is important since the existence of low-lying energy minima involving tetrahedrally coordinated atoms appears to be crucial for ionic conductivity. The openness of the structure is affected not only by the coordination preference of the B-cation but also by the A-cations; Sammells et al. [22] have used the concept of lattice free volume (the unit cell volume minus the total volume of the constituent ions) to rationalize the ionic conductivity of perovskite-type oxides. Larger free volumes for a given substitution degree are thus often associated with higher ionic conductivities. This argument has recently been used to explain the increase in ionic conductivity of $Ba_2In_2O_5$when there is partial substitution of Ba with Sr or La [7] and the decrease in the ionic conductivity of the cubic high temperature phase [8] when there is partial substitution of In by Ga. Still, although the macroscopic correlation is both interesting and useful, a fundamental atomistic understanding of the change in conductivity is needed.

We have previously proposed a structure–activity relationship which connects local structure, disorder and ion conduction for perovskite-related $A_2B_2O_5$ oxides [6]. This correlation focuses on the topography of the potential energy hypersurface for understanding fast-ion conduction and emphasises that a high density of low lying energy minima is a prerequisite for high ionic conductivity. Perovskite-related $A_2B_2O_5$ oxides containing B-atoms that have energetic preference for tetrahedral coordination geometry were considered especially interesting. It is worth noting that for the 36-ion cell used in our studies of $Ba_2In_2O_5$ there are approximately twice as many local structures with 50% tetrahedrally and 50% octahedrally coordinated In-atoms, as local structures based solely on 5-fold coordination. The number of local structures containing 50% square planar entities and 50% octahedral entities are even fewer, approximately 1/3 of the number of structures with 5-fold coordination only [3]. Thus the number of local structures involving different sorts of connectivity patterns within the tetrahedral layers of brownmillerite-related structures is considerably larger than the number of local structures solely based on square pyramids or on square planar and octahedral entities and results in the requested high density of low lying energy minima and thus to many low energy transition pathways for oxygen-ion transport.

The present study identifies *additional* important factors for ionic conductivity. It is most important to note that a high stability of the tetrahedral local environment by itself does not imply fast ion conduction; it is a necessary but not sufficient condition. Ga shows a strong preference for tetrahedral coordination but a number of the brownmillerite-related local structures stable for $Ba_2In_2O_5$ and the Ga and Sr substituted compositions are not stable for $Ba_2Ga_2O_5$. Hence, in addition to preference for tetrahedral coordination [6], the ability to adapt to the many different possible connectivity patterns is important.

It must also be remembered that the availability of many low energy local structures is only one factor that needs to be fulfilled for high ionic conductivity. The conductivity also depends on the barrier heights between different local structures. It seems reasonable to speculate that the local environment in the Ga-substituted case provides an extra barrier to the oxygen transport. With Ga present in the lattice, Ga–O bond lengths have to adjust as part of the oxygen migration process in the conversion of the different tetrahedral patterns, and this provides an extra activation energy.

In addition, the strong preference of Ga for tetrahedral environments clearly hinders transport normal to the two-dimensional layers of the brownmillerite-like structures. Oxygen atoms do not easily migrate from a InO_6-octahedra to a GaO_4-tetrahedra since GaO_5 entities are very high in energy. Again, the energies of the different local structural environments give invaluable information that must be taken into account when considering mechanisms of ion transport. A conventional vacancy jump mechanism requires different types of local short-range order that may be high in energy in a particular system and thus make a negligible contribution. A previously reported example is the consequence of the high energy of the square-planar InO_4 coordination relative to the tetrahedral InO_4 coordination in $Ba_2In_2O_5$ [3].

Finally, it is interesting to note that the density of low energy states correlates with the reported ionic conductivity. $Ba_2In_2O_5$, $Ba_{1.75}Sr_{0.25}In_2O_5$ and $Ba_2In_{1.75}Ga_{0.25}O_5$ all show a high density of low energy local structures and are good ionic conductors. A higher density and a higher ionic conductivity is suggested for $Ba_{1.75}Sr_{0.25}In_2O_5$ than for $Ba_2In_2O_5$. The opposite is indicated for $Ba_2In_{1.75}Ga_{0.25}O_5$ compared to $Ba_2In_2O_5$. Although it is not possible to draw firm conclusions from the compounds considered in this study alone, this observation supports our main hypothesis. That is, a high density of low energy local structures is a prerequisite for high ionic conductivity. In line with this argument the calculations also suggest that the ionic conductivity of $Ba_{1.75}Sr_{0.25}In_2O_5$ is larger than the ionic conductivity of the end-members $Ba_2In_2O_5$ and $Sr_2In_2O_5$, see Fig. 6. This “mixed alkali”-like effect is then related to the variation of the density of low energy local structures along the solid solution series.

Acknowledgement

This work was funded by Norsk Forskningsråd (project number 142995/432). Computational facilities were made available through grants of computer time for the Program for Supercomputing, Norway.

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