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Description/Abstract

Hexagonal aluminate ceramics containing alkaline, alkaline earth and lanthanide elements have been widely investigated, in particular, as superionic conductors, luminescent and laser materials, and radwaste disposal hosts. Recently, there has been some indication that they may be utilized in catalytic converters and in ceramic matrix composite materials for use in high temperature applications, such as jet engines. The structures of these compounds are of either magnetoplumbite (MP) or β-alumina (ß) type both of which consists of spinel-like blocks separated by mirror planes containing the large cations. The major difference between the two structures lies in the composition and site occupancy in these mirror planes which are close-packed in MP but not in β. Although MP's and β's are structurally very similar, it is the differences between them that dominate and lead to their rather different properties. The phase equilibria and crystal chemistry of these complex-structured hexa-aluminates show a considerable variation as a function of composition.

The objective of this study is to determine the energetics of the various defect structures which lead to different relative stabilities of hexa-aluminates, which are found to adopt different crystal structures depending on stoichiometry and chemical composition, by using atomistic computer simulations. Issues of phase stability, which depend on structure/composition relationships, are also of some interest. The work has so far focused on the following subjects: Structural Chemistry of Alkaline Earth Hexa-aluminates, Crystal Chemistry and Defect Structures in Ba Hexa-aluminates, Defect Structures and Non-stoichiometry in Lanthanum Hexa-aluminate, Defect Solid State Chemistry of Lanthanum Magnesium Hexa-aluminate, Defect Structures and Nonstoichiometry in Sodium Lanthanum Hexa-aluminate, Calcium Hexa-Aluminate, and Nd doped β" alumina.

FINAL TECHNICAL REPORT
GRANT # DE-FG02-91ER45451

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Abstract

Work has been completed on the atomistic simulation of hexa-aluminate ceramics with the magnetoplumbite and beta-alumina type structures. In this report, three aspects of the work are highlighted. One is the simulation of surface structures. The second concerns details of the interstitialcy mechanisms observed in molecular dynamics simulations. The novel result here is the observation that the lattice ion always leaves its Beevers-Ross site before the aBR interstitial begins to move towards the lattice site. It is also found that, as expected, the interstitial mechanism is the most common mechanism in the heavily disordered nonstoichiometric structure, as well as in the stoichiometric material. Finally, the disposition of trivalent europium in the phosphor material BAM has been elucidated.

DOE/ER/45451-11

STRUCTURE, STOICHIOMETRY AND STABILITY IN MAGNETOPLUMBITE AND β–ALUMINA STUCTURED TYPE CERAMICS

Final Technical Report

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March 2004

Prepared for

Results

The work completed under this grant is summarized below, in terms of the theses which were produced as a result of the grant:

Structure and Stability of Europium Doped β-Alumina Type Phosphor;
Z. Wu, Ph.D. thesis

Structural and defect properties of β-alumina related barium phases have been investigated with the aid of atomistic computer simulation. The predicted optical behavior of the barium hexa-aluminates doped with Eu^{2+} has been studied and compared. Altogether, five structures have been discussed: $BaMgAl_{10}O_{17}$ (BAM), $Ba_{0.75}Al_{11}O_{17.25}$ (barium-poor end member), $Ba_3Mg_3Al_{30}O_{51}$ (β″ phase), $BaMg_3Al_{14}O_{25}$ (β‴ phase) and $Ba_3Al_{32}O_{51}$ (a hypothetical phase). Intrinsic and extrinsic point defect properties have been calculated for each phase and compared, along with the Mg ion distribution in the spinel blocks and oxygen ion distribution in the conduction planes. Ion migration issues associated with Eu have also been investigated. The dependence on the interatomic potentials used has also been addressed.

Our work has suggested that BAM structures will have two different Mg distributions that will affect the point defect properties. The two possible distributions cannot be distinguished by lattice energy. Both configurations will co-exist in the real materials. Although two Mg distributions exist, the thermally predominant defect, a barium Frenkel defect, is the same for both distributions. The most significant change resulting from the Mg distributions is the oxygen interstitial position. This will reside in the mirror plane to form a two-bridge configuration at the mOB position, if the distribution retains its mirror symmetry. However, if the Mg distribution destroys the mirror symmetry, the oxygen interstitial will remain inside the spinel block, in the half of the spinel block without the Mg. It seems that the charge of the Mg_{Al} defect plays an important role in determining the position of the defect. Calculations of defect complexes and bond valence sums confirm the results that the Eu^{3+} prefers Al(2) sites in the spinel block, instead of the BR sites in the conduction plane favoured by Eu^{2+}, a result which is found to be independent of the potential model used in the calculation.

Ion migration studies suggest that Eu^{3+} can migrate into the spinel block at relatively low temperature with the help of the Mg ions, but that it will not migrate in the conduction plane, where, in contrast, Eu^{2+} and barium show active migration behavior. Oxygen does not undergo long-range migration in the conduction plane, which implies that the formation of $EuMgAl_{11}O_{19}$, as suggested by Shozo et al., would not occur at the temperature where $BaMg(Al_9Eu)O_{17}$ is more likely to be formed instead. Eu^{2+} seems to prefer to form clusters within the BAM structure, which will deteriorate the luminescent efficiency.

The defect properties of the barium-poor phase are different from BAM, because of the absence of Mg and the presence of oxygen interstitials in the conduction plane. The structural and compositional differences change the location of the defects. Eu^{3+} is instead found to occupy the Al(3) site, the other tetrahedral position, rather than the Al(2) site, in order to compensate for the effective negative charges of the oxygen interstitials in the mirror plane. Multiple configurations with different oxygen interstitial arrangements have been found to have very similar lattice energies. The d-band edge

calculation for the europium ion has suggested that the observed, broader and shifted emission band of Eu^{2+} in the barium poor phase, compared to BAM, is the result of the multiple oxygen distributions that will change the ligand field of Eu^{2+}. The change in the ligand field is large enough to broaden and shift the emission band significantly, to account for the two-band configuration that is seen in the measured emission spectrum. Eu^{3+} ions in the aluminum positions in the spinel block will also have the effect of shifting the emission band. The calculation also suggests that the two Mg distributions in BAM will change the emission spectrum to a continuously curved peak instead of a sharp peak.

A hypothetical structure, $Ba_3Al_{32}O_{51}$, with aluminum vacancies inside the spinel blocks seems to have a lower lattice energy than the barium-poor and barium rich phases, but its existence has not yet been demonstrated experimentally. Defect calculations on the $\sqrt{3}$ x $\sqrt{3}$ super-cell of this hypothetical phase show the same defect properties as the barium-poor phase.

Our work has suggested that the barium β'' and β''' phases have defect properties more like BAM than the barium-poor phase, because of similar chemical components and closely related structures. Several structures with different Mg distributions were also found to exist in these two phases. Among all three phases (β β'' and β'''), the β phase (BAM) is the most stable, and hence, presumably, the reason why BAM is widely used rather than the other barium hexa-aluminates. Because of the different environments of the BR sites in the β'' phase, compared to BAM, and because of the possibility of its intergrowth with BAM, our study suggests that the formation of the β'' phase will shift the emission band significantly and degrade the designed emission properties of the BAM:Eu^{2+} phosphor material. Europium ions in the β''' phase also show an emission band shift with respect to BAM but to only a small extent, so there is no large influence of the formation of the β''' phase in the BAM material. Finally, the refinement of the potential parameters to account for the different coordination numbers found for Eu did not affect the results of the calculations.

Atomistic Simulation of Surface Structures and Energies of Alkaline Earth Hexa-aluminates;
D. M. Stohr, Ph.D. thesis

Atomistic computer simulation techniques were used to model five crystal structures in the hexa-aluminate family. Calcium and strontium hexa-aluminates adopt the magnetoplumbite structure. Barium hexa-aluminate phase separates from the theoretical magnetoplumbite structure into the barium β(I)-alumina and barium β(II)-alumina phases because it is thermodynamically unstable, as a result of the large size of the Ba^{2+} cation.

The structure of the crystal influences the morphology of the crystal. Each system modeled resulted in plate-like crystals. It was also determined that the chemistry, in addition to the crystal structure, can lead to differences in the number of low dipole moment termination planes within a given surface orientation and thus differences in their morphology. Calculations performed during this study indicate that each has subtle differences in their final crystal shape. The complexity of these unit cells presents the possibility that planes with initial configurations that relax to the lowest surface energy for a given orientation are missed because they initially possess a dipole moment normal

to the surface. One example where the chemistry of the system changes the morphology of the crystal are the {012} surfaces in the calcium and strontium magnetoplumbite systems. The calcium magnetoplumbite structure has fewer low-dipole moment terminations than the strontium magnetoplumbite system. The extra low-dipole moment termination in the strontium system results in the lowest energy surface structure. This change causes a difference in the crystal morphology between the two crystals.

Calcium magnetoplumbite was used as the initial model system in this study. The {001} surface was found to have the lowest surface energy configuration, as expected from experimental observations of the crystal shape. Manual construction of the termination plane was necessary for this calculation and for the corresponding termination in the strontium and barium systems. {001} surfaces were also found to have the lowest energy for the strontium and barium systems.

The depth of the divalent cation into the {100} calcium magnetoplumbite surfaces is the dominant factor in the calculated surface energy. Smaller depths of the Ca^{2+} positions result in lower surface energies. The system prefers the Ca^{2+} ion in an exposed position in the unrelaxed surface structure. When the Ca cation is not exposed, subsurface relaxations are more difficult to achieve in the dense mirror plane. The constraint of these subsurface relaxations increases the surface energy for a given termination plane.

The coordination numbers of the exposed surface ions in orientations other than the {100} surfaces play a more prominent role than the depth of the divalent cation in the surface structure and thus the surface energy. Since the mirror plane is no longer perpendicular to the surface, the subsurface relaxations in these orientations are not as hindered by the size of the divalent cation. Exposure of the Ca^{2+} ion is not as critical to lower surface energy structures as in the {100} orientations. Dangling O^{2-} ions that occupy low coordinated positions thus become the most important factor in determining which termination, in a family of orientations, has the lowest energy structure.

The metastable surface structures found while modeling the (110) orientation are due to limitations in the simulation software (the METADISE program). Minor differences in the surface vectors cause slight changes in the starting configurations of nominally symmetrically equivalent surfaces. The smaller calculated size of the surface area during reorientation of the unit cell causes an increase in the repulsive energy between neighboring ions and thus a small increase in the surface energy of a given orientation. This does not allow for a complete relaxation of the termination, which should, in principle, result in the same surface structure (and energy) for the symmetrically equivalent orientations. Examination of all of the symmetrically equivalent orientations ensures that the global minimum surface energy structure is found.

The strontium magnetoplumbite system is very similar to the calcium system. The {001} surfaces are again the lowest surface energy orientations. The exposure of the Sr^{2+} ion plays a lesser role in the lowest calculated surface structure. Two factors have been identified as the cause of the difference between the strontium and calcium systems. The first is the more open nature of the spinel blocks due to the larger size of the Sr^{2+} ion. This allows for more subsurface relaxation to occur in these blocks. The second is the higher polarizability of the Sr^{2+} ion. This allows for a greater relaxation, or distortion, of the "electron clouds" on the Sr^{2+} ions. Both the exposure of the divalent cation and the coordination of the surface atoms control the calculated surface structure and energy.

The theoretical barium magnetoplumbite structure has a different space group than the other two structures. The large size of the Ba^{2+} ion causes the O^{2-} ions to rumple in layers near the mirror plane, This rumpling lowers the symmetry of the system. Again, the {001} surface has the lowest energy. The larger size of the Ba^{2+} ion, and thus the unit cell parameters, reduces the differences in the surface vectors for the symmetrically equivalent termination planes. The hindering of the subsurface relaxations due to the large Ba^{2+} ion is offset by the coordination of surface ions, namely the dangling O^{2-} ions.

The calcium and strontium systems show an increase in surface energy with increasing divalent cation size for most surfaces, with {012} being the exception. Subsurface divalent cations in the closely packed mirror plane can hinder the relaxation of the surface ions and thus increase the surface energy for a given orientation. The lower calculated surface energies for the barium magnetoplumbite system are due to the rumpling of the oxygen layers above and below the mirror plane in the bulk structure. The difference between the bulk structure and the relaxed surface structure is smaller in the barium system than in the Ca and Sr systems. Since the surface structure and hence its energy, is closer to the bulk structure, this results in lower surface energies for the Ba magnetoplumbite system compared to the Ca and Sr systems which do not have rumpling. Low coordination of the surface atoms may negate any decreases in energy created by exposing the divalent cation.

The location of the Ba^{2+} ion plays only a minor role in the lowering of surface energies in the β-aluminas. The openness of the mirror plane regions allows subsurface relaxations to occur that would be otherwise lost with the larger cations in the magnetoplumbite structures. The coordination of the surface atoms, mostly the number of dangling O^{2-} ions, and the reduction of polarization in the surface structure have the greatest impact on the surface energy of a given orientation.

The barium β(I) and β(II)-alumina systems have the lowest surface energy for the {001} orientation, as in the magnetoplumbite systems. Unlike in the magnetoplumbite systems, the exposure of the Ba^{2+} ion is not critical for the structure to be the lowest energy termination for any given orientation. This is due to the more open nature of the mirror plane region in these structures. There is more room for subsurface relaxations to occur, even with the large Ba^{2+} ion occupying positions deeper in the surface structure. The coordination of the surface ions, especially the number of dangling O^{2-} ions, and the constraint of relaxation of surface O^{2-} ions, control the calculated surface structure and energy.

One problem that occurs in modeling of these two systems is the high number of calculations that were prematurely ended, i.e. they stopped before reaching a valid minimization. There are two causes for unsuccessful calculations. One is the development of an excessive polarization in the surface structure. The second is a relaxation to a structure that has an increased dipole moment perpendicular to the surface, resulting in a divergent surface energy. Obviously, real surfaces do not have dipole moments normal to the surface.

The calculations showed that stabilization of the barium magnetoplumbite phase in very small crystals is very unlikely. This because the differences in surface energy are not large enough to provide for an overall lower energy for these crystals.

The calculation of surface defects and the prediction of segregation to the surface of dopant cations were also included in this study. It was found that dopant cations that

are smaller than the host surface cation result in a lowering of the surface energy of the defect-containing surface. This is due to the relaxation of the defect cation towards the bulk of the structure, away from the surface. In the case of the Mn^{2+} dopant, the rumpling of the O^{2-} layers and the differences in chemistry between the Mn^{2+} and the alkaline earth cations results, however, in a higher than expected surface defect energy.

The two factors determining whether a defect will occupy a surface position are the segregation energy and the change in surface energy. A positive segregation energy and an increase in the surface energy will always result in a dopant occupying a bulk position. A negative segregation energy and a decrease in the surface energy will always have the dopant occupy a surface position. The size of the crystal can determine if a dopant occupies a surface position for the case when the segregation energy is positive and there is a decrease in the surface energy, and likewise when the segregation energy is negative but there is an increase in the surface energy.

It was found that Mg^{2+}, Mn^{2+} and Ba^{2+} substitution on the divalent cation site always results in a segregation of the dopant to the surface for the {001} orientations. Ca^{2+} and Sr^{2+} defects occupy surface positions in the two barium β-alumina systems for the {001} orientations, but not in the barium magnetoplumbite system. Mn^{3+} substitution for Al^{3+} was never found to occur.

The simplicity of the segregation model approach does have limitations. The segregation of Mn^{3+} to positions on the {001} surface of the barium β(I)-alumina structure is not predicted by this model, since it has a positive segregation energy and the calculated surface energies decrease in the presence of Mn^{3+}. However, experimental results suggest that the Mn^{3+} ions do occupy surface positions.

The possibility o stabilization of the barium magnetoplumbite phase in very small crystals was revisited including surface defects in the model. Five cases for defect surface stabilization were examined. It was found that the barium magnetoplumbite phase cannot be stabilized by the inclusion of surface defects.

Two main features of these surface calculations show the validity of their use in surface science. The calculations predict the experimentally observed plate-like crystal geometries for the alkaline earth hexa-aluminates. Secondly, in the simulations of the {001} surfaces, relaxation of the surface Al^{3+} ions into the surface (towards the bulk) and the rumpling of the basal plane were predicted by the calculations. Similar relaxations were seen in simulations of the surfaces of α-alumina.

The results of this work do show that the atomistic simulation techniques can be use to model surface structures of fairly complicated systems.

Modified Molecular Dynamics Computer Simulations for the study of Transport Phenomena;
R.J. Lewis, M.S. Thesis.

Molecular dynamics serves as a very significant tool, particularly for the study of transport phenomena. However, the mass of data offered is typically of very limited use to the researcher simply because it is couched in terms of atomic coordinates. For the study of transport, intra-site displacements, or thermal fluctuations, represent nothing of any real significance because transport is the result of displacements between sites (or inter-site displacements). The difficulties associated with this fact are exacerbated by

restrictions due to small atomic system size and very short time periods, on the order of a nano-second.

Via an atomic distribution plot, molecular dynamics was used to demonstrate how the simulated atoms within our system have distinct regions in space where the probability of occupation is very large. These regions have been identified as the atomic sites. The coordinates for any given atom at any time step of the simulation can be considered to be but a single measurement of its corresponding site. Our description then defines a site as the result of many such displacements subject to small (i.e. local) random errors. Atomic distribution plots were identified as a means of applying an added potential directly to the atomic site in order to increase the frequency of infrequent events. It was shown that a properly added potential matched the potential well at the boundaries and that it did not result in additional boundaries rivaling the original. However, because transport requires one to define the position of the added potential, the atomic distribution was clearly an unacceptable candidate for such a task.

It was shown that an alternative method of quickly, and reasonable accurately, determining an atomic site position was available. This method involved using N position and force vectors for a given atom, through the use of the Hough Transform, to estimate the coordinates for the so-called "bottom" of the potential well in which the atom resided. The error associated with this estimate for an atomic site was stated to be less than 1/3 of the atomic mean squared displacement (averaged squared displacement of an atom from its average site). This was deemed more than sufficient for the purpose of quickly establishing average site coordinates. With this tool in hand, it was determined that a generalized added potential could be added to each atom type within the system based upon the aforementioned atomic site coordinates.

Application of the added potential is predicated on our ability to detect when a jump occurs. This also depends, as does jump detection, on a well-defined system of atomic sites. It was felt that a considerable advantage could be gained in the analysis of transport phenomena even in the absence of an added potential. Sodium migration in beta-alumina was examined, in some detail, as a means of establishing the nature of this advantage. We first sought some understanding of the specific characteristics of the jump mechanism itself, particularly the specific nature of the interstitialcy mechanism. We were also interested in defining, quantitatively, the role of the extra interstitial ions within the conduction plane. Finally, it was decided to investigate the presence of coordinated interstitialcy jumps within the simulated system.

Through careful study of the jump file it was determined that the BR-site ion always vacated its site prior to the aBR-site ion moving towards the resulting vacancy. The rational lattice site vacancy formation was found to precede the interstitial site "vacancy" formation by an average of 104 time steps (0.208 ps) with a corresponding deviation from that average of 173 time steps (0.346 ps). In all cases that seemed to violate this mechanism, it was demonstrated that the rational lattice ion was found to have moved off the B-R site to a site intermediate between the BR and aBR sites, at some indeterminate previous point in time.

A second interstitial ion was found to be periodically active simultaneously with the original. This condition was in evidence for approximately 14% of the total simulation period. Analysis of the jump file revealed that the A-site defect complex was at times a source and at other times a sink for these secondary interstitial ions. However,

with both conduction planes taken together, never were more than three interstitial ions found to be active simultaneously.

A case was made for the presence of coordinated interstitialcy events. Based upon the average interstitialcy jump duration, a list of four separate spatial configurations of time coordinated jumps along with the average duration and net displacement distances were provided. The significance of coordinated jumping for the study of ionic conductivity was demonstrated.

These simple analyses illustrate the major advantage of treating the system as a collection of atomic sites, rather than as a collection of atoms. However, the main application for which the discussed technique had been developed remained to be investigated. To have quantitative significance, some means was needed of establishing the extent to which a jump sample, for a given length of time, had been increases (another perfectly good way of thinking of this is in terms of an expanded time scale). A plot of the natural logarithm of the number of jumps (scaled to be consistent with a sample accumulated over 1ps) produced a nearly identical plot for simulations run at 500K and 773K. If the phenomenon follows that described in equation 1.3.2 ($N_a' = N\exp(E_a-V_a)/kT)$), then the product of the calculated slope of the fitted line should be unity. The values found were 1.11 for both the 500K and 773K simulations, which is good evidence in support of the quantitative significance of this technique.

Sodium β-alumina may well have been one of the best possible systems to be used as a test subject. The highly disordered nature of the conduction plane is an outstanding challenge of the technique's site determining capabilities. However, the spinel-like regions of Al_2O_3 ensure that the vast majority of ions exist within a highly ordered structure. This fact provides for a very stable set of average site coordinates, which is very good for keeping the system in a steady state condition. As has been discussed, this is because excessive movement of the added potential position is sure to disrupt the system. This may be an obstacle to the use of this technique on a more globally disordered system such as glass. Though, use of the average site coordinates will offset this difficulty quite a bit, since averages can be accumulated over long time periods with no added potential whatever. In any event, the first indication as to such a disruption is a loss in linearity in the values of $\ln(N_a')$ versus V_a. The same thing will occur if the added potential is applied too rapidly. This is the best criterion for establishing proper system behavior under the influence of an added potential.

Status of personnel

Raymond Lewis completed his MS thesis and successfully defended it. Darren Stohr defended his PhD thesis in May 2004. Zhehua Wu defended his PhD thesis in the summer of 2002.

Publications and presentations

A number of presentations have been made of the work supported by this DOE grant. These include the following:

"Point Defect Chemistry of Barium Magnesium Aluminate Phosphors," A.N. Cormack and Z. Wu, Proc. Symposium on Luminescence, The Electrochemical Society Meeting, October 1999.

"Computer Simulation of Point Defect Properties in Barium Magnesium Aluminate Phosphors" ICDIM 2000, Johannesburg, South Africa, 4 April 2000

"Surface Structures in Hexaaluminates with the Magneto-plumbite Crystal Structure" ICDIM 2000, Johannesburg, South Africa, 6 April 2000

"Computer Modelling of Point Defects: A Review" invited talk at the American Ceramics Society Annual Meeting, St. Louis MO, May 2000

"Point Defects in Mg-poor BAM" American Ceramics Society Annual Meeting, St. Louis MO, May 2000

"Molecular Dynamics Simulations of Ion Transport: The Mixed Alkali Effect" AustCeram2000, Meeting of the Australasian Ceramics Society, Sydney, Australia, July 2000

"Modelling the Surface Structure of Glass and Ceramics" Christmas Meeting of the Solid State Chemistry Group pf the Royal Society of Chemistry, Edinburgh University, 18 December 2000.

Work sponsored by DOE was discussed (with due acknowledgement) in a lecture on Modelling Point Defects given to the Jawaharlal Nehru Centre's School on *Computational Techniques for Condensed Matter,* I.I.Sc. Bangalore India, January 2001.

NATO Advanced Study Institute on Computational Materials Science, Tuscany, Italy "Computer Simulations of Glasses" *(invited)* 21 Sept 01

"Molecular dynamics calculation of Ion Migration in BAM" Annual Meeting of the American Ceramic Society, St. Louis, MO. Given by Z. Wu 30 April 02

"Defect Structures and Nonstoichiometry in Lanthanum Hexa-Aluminate," J.G. Park and A.N. Cormack, J. European Ceramic Society, **19**, 2249-56 (1999).

"Defects in $BaMgAl_{10}O_{17}$: Eu^{2+} Blue Phosphor", Z. Wu and A. N. Cormack, J. Electroceramics, **10**, 179-191 (2003)

"Ion Migration in BAM", Z. Wu and A. N. Cormack, in revision for J. Electroceramics

Manuscripts in preparation

Atomistic Simulation of Surface structures and Energetics of Magneto-plumbite type Ca-, Sr- and Ba- hexaaluminates

The structure and energies of various surfaces have been calculated for alkaline earth hexaaluminates with the magnetoplumbite crystal structure. The complexity of this crystal structure gives rise to a large number of possible terminations, which have been studied systematically. The role of the surface structure and energy on stabilizing the magnetoplumbite structure for the barium hexaaluminate is discussed.

Effect of Chemistry on Surface Structures in Magnetoplumbite Structured Hexaaluminates

Although, in principle, strontium and calcium hexaaluminates are isostructural, with the same space group, differences are found in the structures of surfaces with nominally the same orientation. In some orientations, stable structures are predicted for one compound but not for the other.

Atomistic Simulation of the Surface Structure and Energetics of Barium Hexaaluminates

Barium hexa-aluminate does not form a stable magnetoplumbite structure, in contrast to the Sr and Ca hexaaluminates. Instead non-stoichiometric phases based on the beta-alumina structure are formed. The effect of (bulk) structure and stoichiometry on the surface structures have been examined using atomistic computer simulation methods

Atomistic studies of bulk and surface defect structures in calcium hexaaluminate

Surface defects play a key role in controlling surface related properties such as catalysis. A study of surface defects in calcium hexaaluminate has been undertaken using atomistic computer simulation methods. Bulk point defect calculations are presented for comparison.

Eu in β'' and β''' barium hexaaluminates

Although the host crystal structure for BAM is that of β-alumina, other variations, such as the β'' and β''' structures, are believed to be possible contenders and may even co-exist in commercial preparations. Point defect calculations in these other structures have been undertaken for comparison. It is concluded that although there are some differences in the defect energies, the site preferences for Eu in all of these structures is the same.

Eu in barium poor hexaaluminates

The phase equilibrium diagram shows a continuous solid solution between BAM (barium magnesium aluminate) and a magnesium free phase. Thus the compensation mechanism for the incorporation of divalent barium into the b-alumina structure has to change from Mg addition. This is believed to occur through the addition

of oxygen into the mirror plane region, which in turn will affect the mechanism of incorporation of Eu. Atomistic simulation studies show that indeed this is the case.

Sodium Migration Mechanisms in Non-stoichiometric Beta Alumina

Molecular dynamics studies on supercell configurations have been used to investigate the details of sodium migration mechanisms in non-stoichiometric β-alumina, in which the conduction plane is heavily disordered. A new method for probing less common, more highly energetic events has been introduced. The results suggest that the interstitialcy mechanism, thought to be operative in the stoichiometric structure, also operates in the non-stoichiometric structure. Correlations between the mobile species arediscussed.

GRANT NO. DE-FG02-91ER45451

Publications and Presentations

"Ion Migration in BAM", Z.Wu and A. N. Cormack, in revision for J. Electroceramics
"Defects in BaMgAl$_{10}$O$_{17}$:Eu^{2+} Blue Phosphor ", Z. Wu and A. N. Cormack, J. Electroceramics, **10**, 179-191 (2003)
"Molecular dynamics calculation of Ion Migration in BAM" Annual Meeting of the American Ceramic Society, St. Louis, MO. Given by Z. Wu 30 April 02
"NATO Advanced Study Institute on Computational Materials Science, Tuscany, Italy "Computer Simulations of Glasses" *(invited)* 21 Sept 01
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"Point Defect Chemistry of Barium Magnesium Aluminate Phosphors," A.N. Cormack and Z. Wu, Proc. Symposium on Luminescence, The Electrochemical Society Meeting, October 1999.
"Study of Ion Distribution in Nd(III) Doped β" – alumina", submitted to J. Electroceramics.
"Defect Solid State Chemistry of Lanthanum Magnesium Hexa-aluminate", to appear in "Computational Modeling of Materials and Processing", The American Ceramic Society
"Crystal Chemistry of Hibonites with Ideal Composition of CaAl$_{12}$O$_{19}$" will be submitted shortly.
"Defect Structures and Nonstoichiometry in Lanthanum Hexa-aluminate" has been submitted to *Journal of Solid State Chemistry*.
"Defect Energetics and Nonstoichiometry in Lanthanum magnesium Aluminate" has been accepted for publication in *Journal of Solid State Chemistry*.
"Crystal/Defect structures and Phase Stability in Ba Hexa-aluminates" appeared in *Journal of Solid State Chemistry 121,278-290 (1996)*.
"Potential Models for Multi-component Oxides: Hexa-aluminates," appeared in *Philosophical Magazine B73, 21-31 (1996)*.
"Structural Chemistry of Alkaline Earth Hexa-aluminates" appeared in *Solid State Ionics IV: MRS Symposium Proceedings Vol. 369, pp. 457-462 (1995)*.