

# Crystal Defect Chemistry of Strontium Hexaaluminate Magnetoplumbite

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## Abstract

Computer-based atomistic simulation methods are applied to address quantitatively the crystal defect chemistry of strontium hexaaluminate,  $\text{SrAl}_{12}\text{O}_{19}$ . Our calculations show that oxygen Frenkel disorder is the dominant intrinsic defect mode to be expected in the multi-component oxide, though Schottky disorder may also exist. When La and Mg enter into  $\text{SrAl}_{12}\text{O}_{19}$ , Mg prefers to occupy Al(3) 4f tetrahedral sites in the magnetoplumbite structure. Our calculations also indicate that  $\text{O}_{\text{Sr}}$  defect is improbable in the structure.

## 1. Introduction

Hexaaluminates with the magnetoplumbite crystal structure have been receiving considerable attention recently, because of their diverse applications: In particular, luminescent and laser host materials,<sup>1-4)</sup> radioactive waste containers,<sup>5,6)</sup> high temperature combustion catalyst hosts,<sup>7,8)</sup> and substrate materials for rare earth hexaferrite thin films.<sup>9,10)</sup> The actual use of these materials will be dictated, of course, by the details of their solid state chemistry, in particular their defect chemistry.

The composition for an ideal magnetoplumbite phase based on  $\text{Al}_2\text{O}_3$  is  $\text{MAl}_{12}\text{O}_{19}$  (where M is typically an alkaline earth such as Sr or Ca) which has a hexagonal structure, with space group  $P6_3/mmc$ . The unit cell is composed of spinel-structured slabs containing  $\text{Al}^{3+}$  cations separated by mirror planes which contain one  $\text{Sr}^{2+}$  and three oxygen ions per unit cell (Fig. 1); the Wyckoff position of cations and their coordination features are gathered in Table 1.

It has been found that alumina-based magnetoplumbites exhibit a wide range of chemistry and nonstoichiometry whose origin obviously lies in the defect structure of the material. The large divalent cation can be replaced completely by a trivalent cation such as  $\text{La}^{3+}$  or other rare earth species with

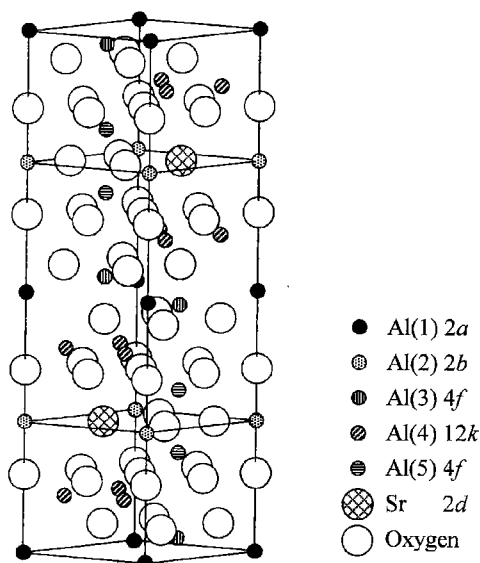


Fig. 1. Unit cell structure of hexaaluminate magnetoplumbite.

compensation by a different cation such as  $\text{Mg}^{2+}$  substitution for  $\text{Al}^{3+}$  in the spinel blocks. Due to the complexity of the basic crystal structure, however, the knowledge of the intrinsic defect structures available from experiment is quite limited. For instance, the distribution of Mg or other small cations over the possible Al sites has not been determined con-

**Table 1. Some characteristics of the different cation sites in the magnetoplumbite structure**

	Wyckoff position	Site symmetry	Coordination
Regular octahedron	Al(1) 2a	D <sub>3d</sub>	6
Trigonal bipyramid	Al(2) 2b	C <sub>3v</sub>	5
Tetrahedron	Al(3) 4f	C <sub>3v</sub>	4
Distorted octahedron	Al(4) 12k	C <sub>s</sub>	6
Antiprism	Al(5) 4f	C <sub>3v</sub>	6

clusively; in fact several different schemes have been proposed.<sup>11,12)</sup>

In one of our earlier simulation studies,<sup>13)</sup> we reported our results on the defect solid state chemistry of SrAl<sub>12</sub>O<sub>19</sub>. However, we have concluded that the potential model used in the earlier study was not sufficiently optimized, as discussed recently.<sup>14)</sup> And we have found that some fundamental conclusions as well as the defect energetics previously reported must be revised. Therefore, in this paper, we are revisiting some of the topics in the earlier work on SrAl<sub>12</sub>O<sub>19</sub>, by applying potential models more optimized than the earlier ones.

## 2. Simulation Techniques

### 2-1. Interatomic Potential Models

The simulations in this study are based on the Born model description of solid, which treats the

solid as a collection of point ions with short-range forces acting between them. The approach has enjoyed a wide range of success, but it has been found that the reliability of the simulations depends on the validity of the potential model used in the calculations.

The short-range potentials are usually described by a simple analytical Buckingham function,

$$V_{ij}(r_{ij}) = A_{ij}\exp(-r_{ij}/\rho_{ij}) - C_{ij}r_{ij}^{-6} \quad (1)$$

where  $r_{ij}$  is the distance between the ions  $i$  and  $j$ . The short-range interaction includes both the repulsive forces due to the overlap of ion charge clouds, and an attractive term due to dispersive interactions. The polarizability of the individual ions constituting the lattice is included through the shell model originally developed by Dick and Overhauser.<sup>15)</sup> This model consists of a simple mechanical representation of the ionic dipole. A massless shell that is connected to the core by a harmonic spring represents the polarizable valence shell electrons.

The potential parameters  $A$ ,  $\rho$ , and  $C$  in Eq. (1), with the shell charges  $Y$ , and spring constant  $k$ , need to be determined for each interaction and ion type in the crystal. The general procedure that we adopted for evaluating potential parameters in complex oxides was to transfer the relevant parameters derived from the simple oxides. In the present study, they were taken from the compilation of Lewis and Catlow<sup>16)</sup>

**Table 2. Interatomic potential parameters used in this study**

Interaction	$A$ (eV)	$\rho$ (Å)	$C$ (eV Å <sup>-6</sup> )
Sr-O	1400.00	0.35000	0.000
Al-O	1474.40 [1334.31] <sup>†</sup>	0.30059	0.000
Mg-O	821.60 [710.50] <sup>†</sup>	0.32420	0.000
La-O	1644.98	0.36196	0.000
O-O	22764.20	0.14910	17.890

<sup>†</sup>Values in brackets are appropriate for cations in a tetrahedral environment.

(ii) Shell model parameters.

Interaction	Shell charge (e)	Spring constant (eV•Å <sup>-2</sup> )
Sr(core)-Sr(shell)	1.260	34.00
Al(core)-Al(shell)	3.000	99999.99
Mg(core)-Mg(shell)	2.000	99999.99
La(core)-La(shell)	3.000	99999.99
O(core)-O(shell)	-2.207	27.29

and are listed in Table 2. The O--O parameters were taken from the work of Catlow,<sup>17)</sup> respectively. The viability of these potential models for hexaaluminates was fully discussed recently.<sup>14)</sup> It was shown that the potential models, considering coordination changes in the spinel blocks, yielded reasonable simulation results for the thermodynamic stability of alkaline earth hexaaluminates.

## 2-2. Perfect Lattice Simulation

The lattice energy is the binding or cohesive energy of the perfect crystal (per unit cell or per formula unit) and is usually defined as the energy that must be released to the ionic crystal to separate its component ions into free ions. It is of central importance in treating thermochemical properties of solids and in assessing the relative stability of different structures. Moreover, its derivatives with respect to elastic strain and displacement are related to dielectric, piezoelectric and elastic constants and phonon dispersion curves.

The lattice energy is calculated in the Born model (for a static lattice) by the relation

$$U = 1/2 \sum \sum V_{ij}, \quad (2)$$

where the total pairwise interatomic potential,  $V_{ij}$ , is given by

$$V_{ij}(r_{ij}) = q_i q_j / r_{ij} + A_{ij} \exp(-r_{ij} / \rho_{ij}) - C_{ij} r_{ij}^{-6}, \quad (3)$$

with the first term representing the Coulombic interactions between species  $i$  and  $j$ , and the last two the non-Coulombic short-range contributions discussed above. The lattice energy is thus calculated exactly, and the only limitations in the procedure arise from a lack of precise knowledge of the interatomic potentials.

Calculations of the crystal energy of the structure under investigation are combined with efficient minimization procedures to determine the equilibrium configuration, which may then be compared with experimental structure. In the lattice energy calculation the Coulomb terms are handled by the Ewald transformation, while short-range terms are summed directly in real space. Summations of the short-range energies are truncated at an interatomic distance after which they may be taken as negligible; in the present calculations a 'cut-off' of 11 Å was used.

The minimization methods employed a second derivative Newton-Raphson procedure.<sup>18)</sup> In our approach, all the atomic coordinates within the unit cell (not just the symmetry independent ones) are allowed to relax finding the minimum energy configuration. During the atomic coordination relaxation, the lattice vectors are kept fixed. After a minimum energy configuration has been found, the lattice vectors are relaxed using elasticity theory and the calculated residual bulk lattice strains, as described by Cormack.<sup>19)</sup> The atomic coordinates are then re-equilibrated with the new lattice vectors. This procedure is repeated iteratively until all remaining strains (both on the lattice vectors and atomic coordinates) have been removed. Once the equilibrium configuration of the crystal structure has been obtained, crystal properties such as elastic, piezoelectric and dielectric constants can be calculated. For details of the simulation techniques, see Reference 20.

## 2-3. Defect Energy Calculations

Calculations of defect structures and energies introduce one vital feature in addition to those for the perfect lattice methods. This is the occurrence of relaxation of lattice atoms around the defect species. The effect is large because the defect generally provides an extensive perturbation of the surrounding lattice, and, in the case of ionic crystals, the relaxation field is long-range as the perturbation provided by the defect is mainly Coulombic in origin.

The theory of defect energy calculation has been outlined by Catlow *et al.*<sup>21)</sup> Basically, the simulation techniques were based on a generalized Mott-Littleton<sup>22)</sup> approach developed by Norgett,<sup>23)</sup> where the important feature is that the crystal surrounding the defect is divided into two regions. The outer region is treated as a polarizable dielectric continuum, while the atomic coordinates of the distorted inner region are explicitly relaxed using appropriate interatomic potentials. Details of this defect simulation techniques can also be found in Reference 20.

## 3. Results and Discussion

### 3-1. Intrinsic Disorder

Computer simulations are an ideal way to approach

intrinsic disorder in these complex systems because each defect can be treated separately and systematically. In  $\text{SrAl}_{12}\text{O}_{19}$ , vacancy and interstitial formation energies are calculated for each of the possible species. From these quantities, the energies per defect for the various possible modes of disorder may be obtained. For  $\text{SrAl}_{12}\text{O}_{19}$ , a number of types of disorder need to be investigated. Schottky disorder, for example, involves a large number of defects, since one formula unit must be removed from the bulk. Thus we are dealing with a Schottky defect containing 32 vacancies! For nonstoichiometry, one needs to consider as well both  $\text{SrO}$  and  $\text{Al}_2\text{O}_3$  Schottky defects. For Frenkel disorder one needs to consider interstitials of each of the three different chemical species in the unit cell in addition to their corresponding vacancies. Once the energies of the defects have been calculated, then the optimal modes of disorder may be found. The defect energies calculated within our equilibrated crystal structure are gathered together in Table 3.

From the calculated energies for cation and anion vacancies and interstitials, we obtain Schottky and Frenkel defect formation energies, which are also given in Table 3 as energies per constituent defect. Note that because the different types of disorder involve varying numbers of defects, comparison in terms of energy per defect is essential. The thermodynamic grounds for this have been discussed elsewhere.<sup>24)</sup>

**Table 3. Calculated defect energies for the basic atomistic defects.**

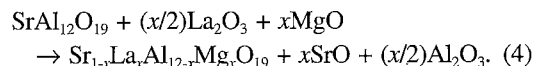
Defect	Defect energy (eV)
$\text{Sr}^{2+}$ vacancy	19.29
$\text{Sr}^{2+}$ interstitial	-5.00
$\text{Al}^{3+}$ vacancy	55.23
$\text{Al}^{3+}$ interstitial	-43.75
$\text{O}^{2-}$ vacancy	22.64
$\text{O}^{2-}$ interstitial	-15.10
$\text{Sr}^{2+}$ Frenkel <sup>†</sup>	7.14
$\text{Al}^{3+}$ Frenkel <sup>†</sup>	5.74
$\text{O}^{2-}$ Frenkel <sup>†</sup>	3.77
$\text{SrO}$ Schottky <sup>†</sup>	4.09
$\text{Al}_2\text{O}_3$ Schottky <sup>†</sup>	3.92
Schottky <sup>†</sup>	3.89

<sup>†</sup>Energy per constituent defect.

Our calculation results indicate that oxygen Frenkel disorder is the dominant intrinsic defect mode to be expected in  $\text{SrAl}_{12}\text{O}_{19}$ . The Schottky disorder may also exist to a somewhat lesser extent.

### 3-2. Cation Substitution in $\text{SrAl}_{12}\text{O}_{19}$

The magnetoplumbite-structured  $\text{SrAl}_{12}\text{O}_{19}$  may be expected to accommodate a diverse chemistry because of the variety of crystallographic sites within the unit cell. The structure is composed of spinel blocks, which have the usual IV and VI coordinated sites for cations, whereas the interspinel layers have rather unusual V-fold sites for small cations. The interspinel layers also provide XII-fold sites to accommodate large cations, which may be monovalent, divalent, or trivalent with balancing charge substituents either in the interspinel layer (i.e.,  $\text{Na}_{0.5}+\text{La}_{0.5}$ ) or in both the interspinel layer and the spinel block (e.g., La and Mg replacing Sr and Al, respectively). The latter reaction can be expressed as



The defect reaction energy for this process is

$$E = E(\text{La}_{\text{Sr}}) + E(\text{Mg}_{\text{Al}}) + E_{\text{lat}}(\text{SrO}) + 0.5E_{\text{lat}}(\text{Al}_2\text{O}_3) - 0.5E_{\text{lat}}(\text{La}_2\text{O}_3) - E_{\text{lat}}(\text{MgO}). \quad (5)$$

Some lattice energies and defect energies related to this question are calculated and given in Tables 4 and 5. The reaction enthalpy is calculated to be -1.02 eV when we consider the binding energy of the two point defects. This negative enthalpy indicates that the defect process is energetically favorable.

There is no question of the location of La ion because of its large ion radius. La can only substi-

**Table 4. Calculated lattice energies of relevant compounds per formula unit.**

Compound	Lattice energy (eV)
$\text{SrO}$	-33.75
$\text{MgO}$	-40.44
$\text{Al}_2\text{O}_3$	-158.78
$\text{La}_2\text{O}_3$	-124.14
$\text{SrAl}_{12}\text{O}_{19}$	-987.62
$\text{LaMgAl}_{11}\text{O}_{19}$	-977.73

**Table 5. Calculated defect energies for substitution in SrAl<sub>12</sub>O<sub>19</sub>**

Defect	Position of Mg	Defect energy (eV)
Mg <sub>Al</sub>	Al(1) 2a	29.72
Mg <sub>Al</sub>	Al(2) 2b	29.82
Mg <sub>Al</sub>	Al(3) 4f	28.90
Mg <sub>Al</sub>	Al(4) 12k	29.93
Mg <sub>Al</sub>	Al(5) 4f	31.09
La <sub>Sr</sub>	-	-18.98
La <sub>Sr</sub> +Mg <sub>Al</sub>	Al(3) 4f	9.61
O <sub>Sr</sub>	-	9.18

tute for Sr, which is in the mirror plane 2d position. However, the question of in which particular Al sites one may find Mg located is not so straightforward. It is not easy to identify Mg<sup>2+</sup> and Al<sup>3+</sup> by X-ray diffraction, for they are indistinguishable in terms of scattering factor, and until now no clear evidence has been found of its location on a particular Al site. From a structural determination of LaMgAl<sub>11</sub>O<sub>19</sub>, Lefebvre *et al.*<sup>11)</sup> suggested that Mg prefers to occupy tetrahedral 4f and octahedral 2a sites; on the other hand, Abrahams *et al.*<sup>12)</sup> inferred that the Mg atoms are located at Al(3) 4f positions, sharing a tetrahedral site equally with Al.

We have calculated the energies of Mg<sub>Al</sub> substitution at different Al sites, and the results for these energies are given in Table 5. They show clearly that Mg ions prefer to occupy Al(3) 4f positions located within spinel block with tetrahedral coordination. This tetrahedral site preference of Mg ions in SrAl<sub>12</sub>O<sub>19</sub> is not altered even when we take into account the defect interaction between Mg<sub>Al</sub> and La<sub>Sr</sub>. Our simulation results are consistent with the experimental results of Abrahams *et al.*<sup>12)</sup> but not with those of Lefebvre *et al.*<sup>11)</sup> The site preference and distribution of Mg in LaMgAl<sub>11</sub>O<sub>19</sub> are discussed in detail in one of our recent simulation studies.<sup>25)</sup>

### 3-3. Feasibility test for O<sub>Sr</sub> defect in SrAl<sub>12</sub>O<sub>19</sub>

In earlier spectroscopic studies on a number of magnetoplumbite-type compounds, "oxygen interstitial at the large cation site" has been postulated to interpret their luminescence data.<sup>26,27)</sup> However, since the site potential of the Sr sites usually precludes occupation of that site by a negatively charged ion,

we have doubted the feasibility of this antisite defect. Therefore, we have examined the feasibility of O<sub>Sr</sub> species. Our simulation results (Tables 3 and 5) suggest that this antisite O<sub>Sr</sub> defect is improbable, at least, as a simple point defect in SrAl<sub>12</sub>O<sub>19</sub>, since its formation energy (9.18 eV) is far greater than the sum (4.19 eV) of the energies of the individual basic defects V<sub>Sr</sub> and O<sub>i</sub>. It is not surprising that a simple O<sub>Sr</sub> defect in SrAl<sub>12</sub>O<sub>19</sub> should be energetically unfavorable, since this type of antisite defects is rare in oxide crystals.

## 4. Conclusions

Computer-based atomistic simulation methods are applied to address quantitatively the defect energetics and crystal chemistry of strontium hexaaluminate magnetoplumbite. Our defect energy calculation results indicate that oxygen Frenkel type disorder is the dominant intrinsic defect mode to be expected in the multicomponent oxide, though Schottky disorder may also exist. It is revealed that when Mg ions replace Al ions in the magnetoplumbite-structured SrAl<sub>12</sub>O<sub>19</sub>, the Mg ions prefer to occupy Al(3) 4f spinel-block tetrahedral sites as they do in MgAl<sub>2</sub>O<sub>4</sub> spinel. It is also found that oxygen interstitial at Sr site, O<sub>Sr</sub> defect, is energetically improbable in SrAl<sub>12</sub>O<sub>19</sub>.

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