

Structure Refinement of $\text{SrAl}_{12}\text{O}_{19}$ Magnetoplumbite Using Energy Minimization Techniques

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Abstract

Computational techniques, based on the minimization of the crystal energy with respect to atomic coordinates, are shown to reproduce successfully complex crystal structures, in this case, strontium hexaaluminate magnetoplumbite, $\text{SrAl}_{12}\text{O}_{19}$. The experimental crystal structure and symmetry of the complex material is well reproduced with our potential models and some crystal physical properties are calculated.

1. Introduction

It has been shown that energy-minimization procedures could accurately predict the structures of a number of transition-metal oxides and multi-component oxides. The techniques are based on energy minimization of ionic coordinates within the unit cell of a perfect crystal structure. Due to recent advances both in computer power and in our understanding of interatomic potentials, the method is now applicable to various classes of inorganic solid including structures with large complex unit cells.

Alkaline earth hexaaluminates such as $\text{SrAl}_{12}\text{O}_{19}$, has a structure of magnetoplumbite (ideal formula $\text{PbFe}_{12}\text{O}_{19}$)¹⁾ having hexagonal symmetry of space group $P6_3/mmc$. It is composed of spinel structured blocks which are stacked together in a manner relating each block to its adjacent blocks by a mirror plane containing the large cations. Each spinel block consists of four close-packed oxygen layers with trivalent cations in both octahedral and tetrahedral sites. The unit cell structure of the Sr hexaaluminate can be found in our subsequent paper in this volume.

In one of our earlier simulation studies,²⁾ we reported our results on the defect solid state chemistry of the complex-structured $\text{SrAl}_{12}\text{O}_{19}$. However, we have concluded that the potential model used in the

earlier study was not sufficiently optimized, as discussed recently.³⁾ And we have found that there is a need to revise the earlier results. Therefore, in this paper, we are reporting the perfect lattice simulation results on the structure and crystal physical properties of $\text{SrAl}_{12}\text{O}_{19}$ by applying potential models more optimized than the earlier ones. The crystal defect chemistry of the material is revisited in the subsequent paper in this volume.

2. Simulation Methods

The atomistic lattice simulation techniques in this work are based on the Born model of the solid as we have used and described previously.⁴⁾ In brief, the ionic solid is treated as a collection of point ions with short-range forces acting between them. The lattice interactions, as defined through interatomic pair potentials, are calculated explicitly and ions are relaxed to zero force using a second derivative Newton-Raphson minimization procedure. The electronic polarization effects of the lattice are taken into account by means of the Dick-Overhauser shell model. Details of the energy minimization techniques and related potential models used in this study can be found in our subsequent paper in this volume.

3. Results and Discussion

In the present study, for $\text{SrAl}_{12}\text{O}_{19}$, the structure reported by Lindop *et al.*,⁵⁾ was used both for comparison and as an initial setup for the calculations. The program METAPOCS⁶⁾ was used to determine the equilibrium positions for atoms in the structure. With the X-ray data as the starting point, the lattice energy was evaluated to constant pressure; that is, the bulk lattice strains were removed by allowing the initial lattice vectors of the structure to relax. The new lattice vectors and coordinates generated by our calculation were compared with initial X-ray data in Table 1. From this table we can see that the experimental coordinates and those obtained for the equilibrated structure are in excellent agreement. Note that those coordinates constrained by the symmetry of the space group were not so constrained in

Table 1. A comparison of the final equilibrated structural parameters with the data available in X-ray literature⁵⁾ for $\text{SrAl}_{12}\text{O}_{19}$

Cell parameters		Experimental			Calculated
		<i>a</i>	<i>b</i>	<i>c</i>	Δ^a
<i>a</i>	<i>a</i>	5.562 Å	5.658 Å		
	<i>c</i>	21.972 Å	21.668 Å		
Space group		$P6_3/mmc$	$P6_3/mmc$		
Atom	Site	Coordinates		Δ^a	
Sr	2 <i>d</i>	x	0.6667	0.6667	0.0000
		z	0.2500	0.2500	0.0000
Al(1)	2 <i>a</i>	x	0.0000	0.0000	0.0000
		z	0.0000	0.0000	0.0000
Al(2)	2 <i>b</i>	x	0.0000	0.0000	0.0000
		z	0.2500	0.2500	0.0000
Al(3)	4 <i>f</i>	x	0.3333	0.3333	0.0000
		z	0.0276	0.0311	0.0035
Al(4)	12 <i>k</i>	x	0.1685	0.1681	-0.0004
		z	-0.1082	-0.1077	0.0005
Al(5)	4 <i>f</i>	x	0.3333	0.3333	0.0000
		z	0.1903	0.1883	-0.0020
O(1)	4 <i>e</i>	x	0.0000	0.0000	0.0000
		z	0.1481	0.1474	-0.0007
O(2)	4 <i>f</i>	x	0.3333	0.3333	0.0000
		z	-0.0538	-0.0529	0.0009
O(3)	6 <i>h</i>	x	0.1822	0.1829	0.0007
		z	0.2500	0.2500	0.0000
O(4)	12 <i>k</i>	x	0.1552	0.1543	-0.0009
		z	0.0523	0.0520	-0.0003
O(5)	12 <i>k</i>	x	0.5025	0.5006	-0.0019
		z	0.1476	0.1444	-0.0032

^aDifference between calculated and experimental coordinates.

Table 2. Calculated bulk crystal properties of $\text{SrAl}_{12}\text{O}_{19}$

Lattice energy (eV, per unit cell)	-1975.24
Elastic constants (10^{11} dyne/cm ²)	
C_{11}	55.18
C_{33}	40.16
C_{44}	12.24
C_{12}	23.83
C_{13}	14.79
Static dielectric constants	
$\epsilon(0)_{11}$	7.25
$\epsilon(0)_{33}$	20.64
High frequency dielectric constants	
$\epsilon(\infty)_{11}$	2.67
$\epsilon(\infty)_{33}$	2.80

our calculation. Nevertheless the space group symmetry $P6_3/mmc$ is conserved during the relaxation. We can also see that our potential model generates the experimentally measured cell parameters with reasonable accuracy: Discrepancy between the calculated cell parameters and the experimental values is within 2%. The success of these calculations in correctly reproducing the complex magnetoplumbite crystal structure provides partial support for the viability of the potential models used in the study.

Once the equilibrium configuration of the crystal structure has been obtained, crystal properties such as elastic, piezoelectric and dielectric constants can be calculated: Derivatives of the lattice energy with respect to elastic strain and displacement are related mathematically to those properties. Some typical physical properties of $\text{SrAl}_{12}\text{O}_{19}$ calculated from the equilibrated structure are listed in Table 2. Due to the lack of experimental data in the literatures we cannot compare the calculated properties with the measured values at the moment. However, we expect that the predicted values may be reasonable approximations to the real values.

4. Conclusions

We have shown that it is possible to model complicated crystal structures such as $\text{SrAl}_{12}\text{O}_{19}$ magnetoplumbite using atomistic simulation methods coupled with energy minimization techniques. The experimental crystal structure and symmetry of the com-

plex material is well reproduced with our potential models. Elastic and dielectric constants of the bulk crystal are calculated.

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References

- 1) Adelskold, V., *Ark. Kemi. Mineral. Geol. Mater.*, A **12**, 1 (1938).
- 2) Xie, L. and Cormack, A. N., *J. Solid State Chem.*, **83**, 282 (1989).
- 3) Park, J.-G. and Cormack, A. N., *Philos. Mag. B*, **73**, 21 (1996).
- 4) Park, J.-G. and Cormack, A. N., *J. Solid State Chem.*, **121**, 278 (1996).
- 5) Lindop, A. J., Matthews, C. and Goodwin, D. W., *Acta Crystallogr. B*, **31**, 2940 (1975).
- 6) Catlow, C. R. A., Cormack, A. N. and Theobald, F., *Acta Crystallogr. B*, **40**, 195 (1984).