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Analysis of the ferroelectric phase transition in $BaAl_2O_4$ by group theoretical methods and first-principles calculations

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Group theoretical methods are applied to a ferroelectric phase transition in barium aluminate ($BaAl_2O_4$). The atomic displacements from x-ray-diffraction data are decomposed into four modes: a primary order parameter and three secondary order parameters. The spontaneous polarization P_s is shown to arise from a secondary order parameter, resulting in a very small value of P_s, as is typical of other improper ferroelectrics. Using a first-principles computational method, we show that the primary order parameter becomes unstable, and is driven to a nonzero value at the phase transition. Through coupling, the nonzero primary order parameter then drives the secondary order parameters to nonzero values as well.

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I. INTRODUCTION

Barium aluminate ($BaAl_2O_4$) exhibits a ferroelectric (FE) phase transition at $T_c = 396$ K.[1–3] It belongs to the family of stuffed tridymites which are derived from the structure of SiO_2 β tridymite. Corner-sharing AlO_4 tetrahedra form a three-dimensional network with hexagonal channels which are filled with Ba atoms (for example, see Fig. 2 of Ref. 4).

The structure of the low-temperature FE phase was determined by x-ray single-crystal[5] (hereafter referred to as simply Hörkner data) and powder data[2,3] (hereafter referred to as simply Huang data). The space-group symmetry of the FE phase was found to be #173 $P6_3$. Huang also measured the spontaneous polarization in the FE phase, and found it to be very weak.

Recently, Abakumov *et al.*[4] (hereafter referred to as simply Abakumov) studied the phase transition by transmission electron microscopy. They found that the phase transition evolves over a wide temperature range of 400–670 K, and is accompanied by a doubling of the hexagonal lattice parameter *a* (the FE unit cell is four times larger). They proposed that the space-group symmetry of the high-temperature paraelectric (PE) phase be #182 $P6_322$.

In this paper, we apply group theoretical methods to obtain the primary and secondary order parameters of the PE-FE phase transition in $BaAl_2O_4$. Using first-principles calculations, we show that the primary order parameter is unstable in the PE phase, and drives the transition to the FE phase. The secondary order parameters, including the spontaneous polarization, become nonzero because of their anharmonic coupling with the primary order parameter. The phase transition is thus improperly ferroelectric, resulting in a small spontaneous polarization. Our results are in disagreement with those of Huang, where the polarization fields are treated as primary order parameters.

II. STRUCTURE OF THE PE PHASE

The structure of the PE phase has not been directly determined by x-ray diffraction. However, we can derive a probable structure from the known FE structure if we assume that the PE cell dimensions in the *ab* plane are half those of the FE cell and if we move atoms to the most symmetric sites possible. Restricting atomic displacements to small values, we obtain the maximum possible space-group symmetry to be #182 $P6_322$, in agreement with Abakumov.

In this proposed structure, the lattice parameters are $a = 5.224$ Å and $c = 8.793$ Å with atomic positions given by

Ba $2b$ $0, 0, \frac{1}{4}$,
Al $4f$ $\frac{1}{3}, \frac{2}{3}, 0.0575$,
O1 $2c$ $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$,
O2 $6g$ $0.3521, 0, 0$.

We derive these values from the FE structure data of Huang (see Table 1 in Ref. 2). In obtaining these values, we neglect changes in volume and any other symmetry-preserving distortions that may occur at the phase transition.

III. ORDER PARAMETERS

In the PE-FE phase transition, some of the AlO_4 tetrahedra become tilted about axes in the *ab* plane, resulting in a doubling of the cell dimensions in the *ab* plane and a loss of the twofold axes that lie in the *ab* plane. This reduces the symmetry to $P6_3$, and allows the appearance of a spontaneous polarization field P_s along the *c* axis.

We applied group theoretical methods to this phase transition using the computer program ISOTROPY, developed by Stokes and Hatch.[6] We found that four irreducible representations (irreps) of $P6_322$ are involved: M_2, M_1, Γ_2, and Γ_1 (using the notation of Miller and Love[7]). This means that the atomic displacements which occur during the transition can be decomposed into four modes that have the symmetry of basis functions of these four irreps, respectively. We will simply call these the M_2, M_1, Γ_2, and Γ_1 modes.

The time-averaged amplitudes of the M_2, M_1, Γ_2, and Γ_1 modes are the order parameters of the phase transition. We denote these order parameters by η_1, η_2, η_3, and η_4, respectively. In the PE phase, these modes are vibrational

TABLE I. Atomic displacements in the PE-FE phase transition. Positions are given for atoms in the FE structure (space group $P6_3$) using the data of Huang (and his reported uncertainties). Atomic positions are given in the usual dimensionless units in terms of the lattice constants. The net displacement along with the components of the displacement that contribute to the M_2, M_1, and Γ_2 modes are given in columns 4–7. All displacements are given as multiples of 0.001 (in our dimensionless units), so that the table is easier to read. Note that the net displacement is equal to the sum of the displacements in the M_2, M_1, and Γ_2 modes (± 1 due to round-off of each entry to the nearest 0.001 dimensionless units). In the last column, we give the relative displacements obtained from SCAD for the unstable M_2 mode. (They have been scaled to match the experimental values as closely as possible.)

Atom	Site	Position	Net	M_2	M_1	Γ_2	M_2 (SCAP)
Ba1	2*a*	0, 0, 1/4	0,0,0	$0,0,\bar{7}$	0,0,0	0,0,7	0,0,0
Ba2	6*c*	0.5043(4), 0.0024(7), 0.2594(7)	4,2,9	3,0,2	1,2,0	0,0,7	$\bar{1},0,0$
Al1	6*c*	0.1586(83), 0.3352(40), 0.0609(33)	$\bar{8},2,3$	$\bar{8},2,2$	0,0,1	0,0,1	$\bar{3},0,2$
Al2	6*c*	0.1555(81), 0.3307(40), 0.4442(31)	$\overline{11},\bar{3},2$	$\overline{11},\bar{2},1$	$\bar{1},0,\bar{1}$	0,0,1	$\bar{3},0,2$
Al3	2*b*	1/3, 2/3, 0.9416(70)	$0,0,\bar{1}$	$0,0,\bar{4}$	0,0,3	0,0,1	$0,0,\bar{6}$
Al4	2*b*	1/3, 2/3, 0.5517(60)	$0,0,\bar{6}$	$0,0,\bar{4}$	$0,0,\bar{3}$	0,0,1	$0,0,\bar{6}$
O1	6*c*	0.182(9), 0.006(8), 0.987(8)	$6,6,\overline{13}$	$1,2,\overline{17}$	3,0,0	2,4,4	$0,\bar{1},\overline{10}$
O2	6*c*	0.674(10), 0.001(8), 0.030(10)	$\bar{2},1,30$	$\bar{2},\bar{3},27$	$\bar{3},0,0$	2,4,4	$0,\bar{1},28$
O3	6*c*	0.492(10), 0.169(10), 0.997(9)	$\bar{8},\bar{7},\bar{3}$	$\bar{1},\bar{3},\bar{5}$	$\bar{3},\bar{2},\bar{2}$	$\bar{4},\bar{2},4$	$0,0,\bar{9}$
O4	6*c*	0.180(10), 0.502(14), 0.000(9)	4,2,0	$3,1,\bar{5}$	$\bar{2},\bar{3},2$	2,4,4	$0,0,\bar{9}$
O5	6*c*	0.119(2), 0.304(6), 0.252(9)	$\overline{48},\overline{29},2$	$\overline{33},0,1$	$\overline{15},\overline{30},0$	0,0,1	$\overline{32},0,2$
O6	2*b*	1/3, 2/3, 0.748(10)	$0,0,\bar{2}$	$0,0,\bar{3}$	0,0,0	0,0,1	$0,0,\bar{7}$

modes centered about the equilibrium positions of the atoms, and the order parameters are zero. At the phase transition, the order parameters become nonzero.

We separate the order parameters into primary and secondary types. η_1 (mode M_2) is the primary order parameter, and determines the entire change of symmetry from $P6_322$ to $P6_3$. The symmetry of the M_2 modes is $P6_3$ so that even if only the M_2 mode were present, the symmetry would still change to $P6_3$. η_2, η_3, and η_4 are secondary order parameters. None of these by themselves would change the symmetry all the way to $P6_3$. The symmetry of the M_1, Γ_2, and Γ_1 modes are $P6_322$ (with an enlarged cell), $P6_3$ (without cell enlargement), and $P6_322$ (without cell enlargement), respectively. (We easily obtain these symmetries from ISOTROPY.)

Using group theoretical methods (with the aid of ISOTROPY), we obtain the form of the Landau free energy expanded in powers of the order parameters:

$$\begin{aligned} F = {} & F_0 + F_{12}\eta_1^2 + F_{14}\eta_1^4 + F_{22}\eta_2^2 + F_{23}\eta_2^3 + F_{24}\eta_2^4 \\ & + F_{32}\eta_3^2 + F_{34}\eta_3^4 + F_{42}\eta_4^2 + F_{43}\eta_4^3 + F_{44}\eta_4^4 \\ & + A_{12}\eta_1^2\eta_2 + A_{13}\eta_1^3\eta_3 + A_{14}\eta_1^2\eta_4 . \end{aligned} \tag{1}$$

We truncated the expansion to the fourth degree, and included only those coupling terms which were linear in the secondary order parameters.

Now we can see how the phase transition proceeds. At the transition temperature, the coefficient F_{12} becomes negative, causing the minimum of F to occur at some nonzero value of η_1. Since the coupling terms are linear in η_2, η_3, and η_4, the free energy can be further lowered by allowing η_2, η_3, and η_4 to each become nonzero as well. Thus the instability at the phase transition causes the primary order parameter to become nonzero, which in turn, through coupling terms, causes the secondary order parameters to become nonzero. In other words, the M_2 vibrational mode becomes unstable, which in turn causes the M_1, Γ_2, and Γ_1 modes to become unstable as well.

Note that the presence of coupling terms linear in the secondary order parameters causes the secondary order parameter to participate in the phase transition. Such coupling terms are always present for any mode with a symmetry greater than or equal to $P6_3$. This result illustrates a symmetry principle that can be applied to all phase transitions: given a transition which reduces the space-group symmetry from G to G', every atomic displacement mode which has a symmetry G'' greater than or equal to G' ($G'' \supseteq G'$) must take part in the transition, even if only to a very small degree.[8]

IV. ATOMIC DISPLACEMENTS

In Table I, we give the atomic positions in the FE structure from Huang. We also give the atomic displacements which occur in the transition (column labeled "Net"). This is simply the difference between the positions in the FE structure given in the table and the positions in the PE structure which we derived from the FE structure. We then decompose these displacements into M_2, M_1, and Γ_2 modes. (The Γ_1 mode preserves the original $P6_322$ symmetry. We derived the PE structure ignoring all such symmetry-preserving distortions, since they cannot be obtained from symmetry principles alone. Thus, by construction, there is no Γ_1 mode present in the atomic displacements given in the table.) Again, information obtained from ISOTROPY about the patterns of atomic displacements present in each mode greatly facilitated this decomposition.

We see from Table I that the greatest contributions to the total displacements come from the M_2 mode, as expected, since it is the primary order parameter. The greatest displacements occur for the oxygen atoms, O1, O2, and O5. The AlO_4 tetrahedra to which these oxygen ions belong tilt approximately 9°, about axes which are nearly along the A11-O4 and Al2-O3 bonds, as pointed out by Abakumov (see Fig. 2 in Ref. 4).

A spontaneous polarization field arises from the unstable Γ_2 mode. (The total displacive dipole moment in the unit cell is nonzero. See the *z* component of the atomic displacements for this mode in Table I). Since this is a secondary order parameter, $BaAl_2O_4$ is called an improper ferroelectric. In contrast, Huang's model predicted that $BaAl_2O_4$ is a proper ferroelectric with the polarization fields as primary order parameters.

V. FIRST-PRINCIPLES CALCULATION

We investigated the instability of the M_2 mode using a first-principles calculation. The computer program SCAD, developed by Boyer, Mehl, and Stokes,[9–15] uses a density-functional method to calculate the ground-state energy per unit cell in crystalline solids. These calculations are first principles with no adjustable parameters.

There are 12 triply degenerate M_2 vibrational modes in the PE phase of $BaAl_2O_4$. We calculated the frequency and atomic displacement patterns in each of these modes using the method of frozen phonons. This required calculating the energy of 78 different patterns of atomic displacements. We found that one of the twelve modes is unstable (imaginary frequency). In Table I we show (“M_2 SCAD” column) the atomic displacements in this calculated unstable mode. As can be seen, the greatest atomic displacements in that mode occurred for the oxygen atoms, O1, O2, and O5, in agreement with the experimentally determined displacements given in the “M_2” column of the table. With the exception of Ba2, all of the data in the “M_2 SCAD” column of the table agrees with the data in the “M_2” column to within experimental uncertainty (which is given in the “Position” column). The agreement is actually quite remarkable, considering the fact that the calculations were based on first principles with no adjustable parameters.

We also used SCAD to investigate the stability of the Γ_2 modes responsible for the spontaneous polarization. We found all four of the Γ_2 modes to be stable in the PE phase. This is in agreement with our model. The Γ_2 mode is not unstable in and of itself. The displacements in this mode only occur in response to the unstable M_2 mode. That is the distinction between a primary order parameter (the M_2 mode) and a secondary order parameter (the Γ_2 mode).

VI. SPONTANEOUS POLARIZATION

The spontaneous polarization P_s in the FE phase of $BaAl_2O_4$ is very weak. Huang reported a maximum value $P_s \approx 0.08\ \mu C/cm^2$ at about 200 K for a single crystal. (This was obtained from pyroelectric measurements using the depolarization method.) For comparison $P_s \approx 26\ \mu C/cm^2$ in $BaTiO_3$ (Ref. 16) and $P_s \approx 57\ \mu C/cm^2$ in $PbTiO_3$.[17] Note, however that these are proper ferroelectrics whereas $BaAl_2O_4$ is an improper ferroelectric, i.e., P_s is not the primary order parameter in $BaAl_2O_4$. The value of P_s in improper ferroelectrics is typically smaller. For example, $P_s \approx 1.6\ \mu C/cm^2$ in $SrTiO_3$. (Ref. 18) and $P_s \approx 1.8\ \mu C/cm^2$ in $Tb_2(MoO_4)_3$.[19] Other improper ferroelectrics exhibit even smaller values: $P_s \approx 0.07\ \mu C/cm^2$ in $Tl_2Cd_2(SO_4)_3$ (Ref. 20) and $P_s \approx 0.08\ \mu C/cm^2$ in $Mg_3B_7O_{13}Cl$.[19] We conclude that when compared to other improper ferroelectrics, the value of P_s in $BaAl_2O_4$ is on the small side, but not unexpectedly small.

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