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## Lattice Dynamics of Antiperovskite Structure Compounds $A_3OX$ ( $A = Na, K$ ; $X = Cl, Br$ )

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The phonon spectra, Born effective charges, dielectric constants  $\epsilon_\infty$  and elastic modules of  $Na_3OCl$ ,  $Na_3OBr$ ,  $K_3OCl$  and  $K_3OBr$  have been calculated by the generalized Gordon-Kim method. In the phonon spectra of  $Na_3OCl$ ,  $K_3OCl$  and  $K_3OBr$  unstable modes are found.

**Keywords:** Antiperovskite; phonon spectra; dynamic charges

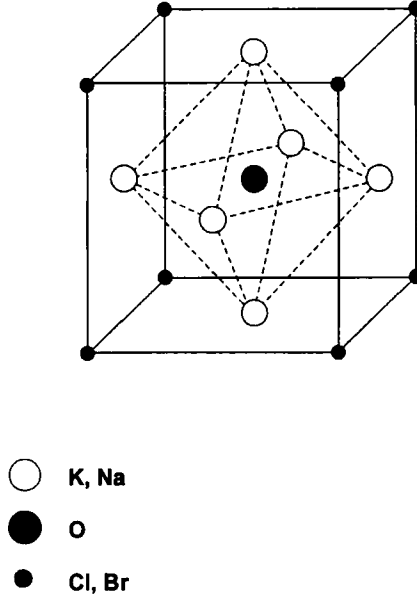
The structural phase transitions and an origin of lattice instabilities in perovskite compounds  $ABX_3$  are studied both experimentally and theoretically during several decades. Many theoretical studies have been performed on perovskite structure oxides. The calculations of the ground-state electronic properties, lattice dynamics and statistical mechanics of the phase transitions in the framework of density-functional theory (DFT) by both LAPW (see, for example, [1–3]) and *ab initio* pseudopotential (see, for example, [4–6]) methods were very successful. As a result, there has been considerable progress in achieving an understanding of the ferroelectricity and antiferroelectricity. In particular, analysis of the charge densities and densities of states showed that the ferroelectric instability is due to the hybridization between oxygen 2p and cation 3d states.

In perovskite structure halogenides structural phase transitions arise as a rule, because of non-polar antiferrodistortive lattice instabilities.

The number of antiperovskites  $A_3OX$ , where the positions of anions and cations are reversed from normal perovskites (Fig. 1), is smaller than that

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**Figure 1.** Unit cell of antiperovskite  $M_3OX$ .

of normal perovskites and the experimental data for physical properties of these compounds are poor.

In this paper we calculate the phonon spectra, dynamic charges, elastic modules and dielectric constants of  $Na_3OCl$ ,  $Na_3OBr$ ,  $K_3OCl$  and  $K_3OBr$  by the Gordon-Kim method in the framework of the microscopic model of an ionic crystal.

The model of the ionic crystal proposed by Ivanov and Maksimov [7], which takes into account the polarizability and deformability of ions, is used to compute the phonon spectrum. In this model the ionic crystal is represented as consisting of individual intersecting spherically symmetrical ions. The total electron density of the crystal in this case can be written

$$\rho(\mathbf{r}) = \sum_i \rho_i(\mathbf{r} - \mathbf{R}_i),$$

where summarization is carried out over all the ions of the crystal. The total energy of the crystal, taking into account only pairwise interactions,

has the form

$$E_{cr} = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \sum_i E_i^{\text{self}}(R_w^i) + \frac{1}{2} \sum_{i \neq j} \Phi_{ij}(R_w^i, R_w^j, |\mathbf{R}_i - \mathbf{R}_j|), \quad (1)$$

where  $Z_i$  is the charge of the  $i$ th ion,

$$\Phi_{ij}(R_w^i, R_w^j, |\mathbf{R}_i - \mathbf{R}_j|) = \mathbf{E}\{\rho_i(\mathbf{r} - \mathbf{R}_i) + \rho_j(\mathbf{r} - \mathbf{R}_j)\} - \mathbf{E}\{\rho(\mathbf{r} - \mathbf{R}_i)\} - \mathbf{E}\{\rho(\mathbf{r} - \mathbf{R}_j)\}, \quad (2)$$

energy  $\mathbf{E}\{\rho\}$  is calculated by electron-gas method [7] using the local approximation for kinetic and exchange-correlation energies, and  $E_i^{\text{self}}(R_w^i)$  is self-energy of ion. The electron density of the individual ion and its self-energy are calculated taking into account the crystal potential, approximated by a charged sphere (the Watson sphere)

$$v(r) = \begin{cases} Z_i^{\text{ion}}/R_w & r < R_w \\ Z_i^{\text{ion}}/r & r > R_w, \end{cases} \quad (3)$$

where  $R_w$  is the radius of the Watson sphere. Radii  $R_w^i$  of the spheres at individual ions are found by minimizing the total energy of the crystal.

To calculate the lattice dynamics in the expression for the energy of the crystal, Eq. (2), it is necessary to add terms that describe the energy changes caused by displacing the ions from their equilibrium positions. When the frequencies of the lattice vibrations of the ionic crystal were calculated, the electronic polarizability of the ions and the “breathing” of the ions in the crystal environment were taken into account. The expression for dynamic matrix is described in [8].

The equilibrium values of the unit cell parameters were determined by minimizing the total energy of the crystal as a function of volume. The lattice parameters are shown in Table I along with the experimental data. Table I shows the calculated elastic constants, polarizabilities of the ions, dielectric constants  $\epsilon_\infty$ , and dynamic charges. For halogen ions the effective charge tensor is isotropic and its value quite close to the nominal ionic charge. In the case of  $\text{Na}_3\text{OCl}$  and  $\text{Na}_3\text{OBr}$  the value of oxygen effective charge slightly differs from the nominal ionic charge, but in the case of  $\text{K}_3\text{OCl}$  and  $\text{K}_3\text{OBr}$  the oxygen effective charge is more than twice as large as nominal one. For alkali metal ions there are two independent

**TABLE I** Equilibrium values of the lattice parameters  $a_0$ (Å), elastic constants ( $10^{11}$  dynes · cm<sup>-2</sup>), Born effective charges  $Z^*$ , the dielectric constants  $\epsilon_\infty$  and the polarizabilities of the ions  $\alpha$  (Å<sup>3</sup>).

	Na <sub>3</sub> OCl	Na <sub>3</sub> OBr	K <sub>3</sub> OCl	K <sub>3</sub> OBr
$a_0$ (calc.)	4.31	4.36	4.76	4.81
$a_0$ (exp.)	4.50 <sup>a</sup>	4.57 <sup>a</sup>	—	5.21 <sup>b</sup>
$C_{11}$	6.0	5.6	3.1	3.9
$C_{12}$	1.2	1.3	0.6	1.0
$C_{44}$	1.5	1.7	0.7	1.0
$Z^*$ (Br, Cl)	-0.93	-0.86	-1.03	-0.95
$Z^*$ (O)	-2.10	-2.16	-4.22	-4.82
$Z_\perp^*$ (K, Na)	1.11	1.11	1.26	1.37
$Z_\parallel^*$ (K, Na)	0.81	0.79	2.72	3.03
$\epsilon_\infty$	2.11	2.20	3.35	4.17
$\alpha_{\text{Br, Cl}}$	2.90	3.46	3.04	4.12
$\alpha_{\text{O}}$	1.59	1.59	2.73	3.10
$\alpha_{\text{K, Na}}$	0.10	0.10	0.68	0.68

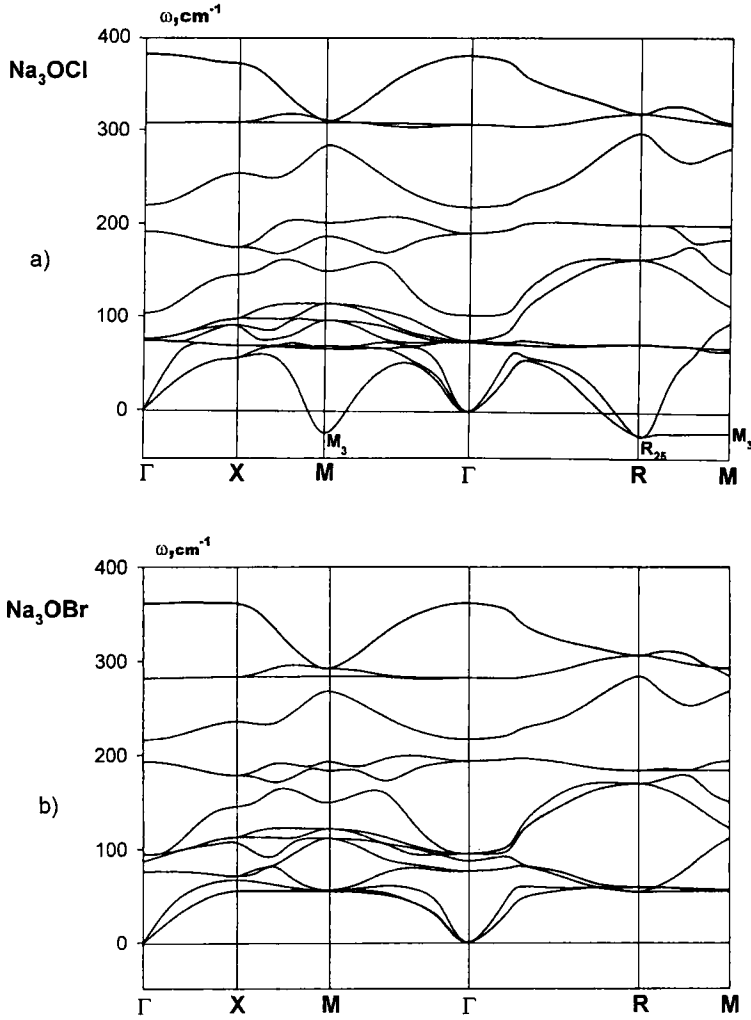
<sup>a</sup>Ref. [9].

<sup>b</sup>Ref. [10].

components of the tensor corresponding respectively to a displacement of the ion  $A^{+1}$  parallel  $Z_\parallel^*(A)$  and perpendicular  $Z_\perp^*(A)$  to the A—O bond. In the case of compounds with sodium the values  $Z_\parallel^*$  and  $Z_\perp^*$  slightly differ from each other and from the nominal ionic charge, but in the case of potassium compounds there is a strong difference between  $Z_\parallel^*(K)$  and  $Z_\perp^*(K)$  like in the perovskite structure oxides, but the value of  $Z_\parallel^*(K)$  is smaller than  $Z_\parallel^*(O)$ .

The calculated phonon dispersion curves of the crystals under consideration are shown in Figs. 2 and 3. The mode frequencies at points  $\Gamma(0,0,0)$  are shown in Table II.

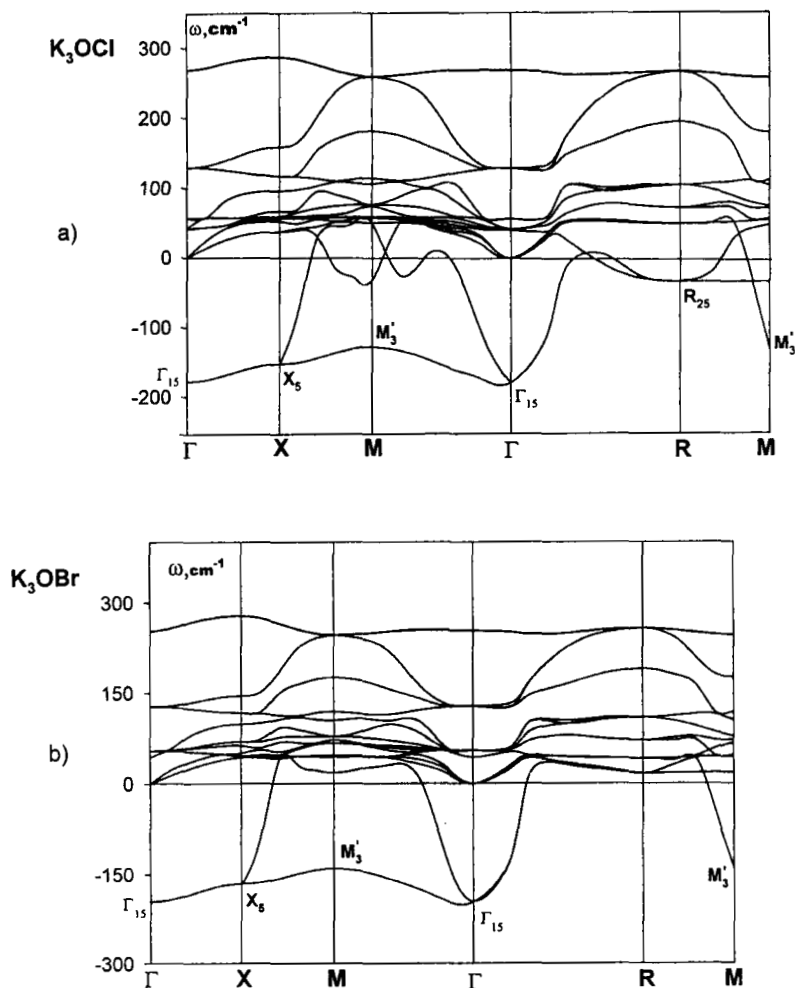
As can be seen in Figs. 2 and 3 and in Table II there are no imaginary frequencies in the phonon spectrum of Na<sub>3</sub>OBr. In the calculated phonon spectra of other compounds unstable modes are present. In the case of Na<sub>3</sub>OCl our calculation indicates unstable modes at the R-point ( $R_{25}$ ) and M-point ( $M_3$ ). These instabilities are of the antiferrodistortive type. The motion of sodium ions in these modes leads to a "rotation" of the octahedra ONa<sub>6</sub>. In the cases of K<sub>3</sub>OCl and K<sub>3</sub>OBr calculations indicate unstable modes at R-point ( $R_{25}$ ), X-point ( $X_5$ ), M-point ( $M'_3$ ),  $\Gamma$ -point ( $\Gamma_{15}$ ) and at X-point ( $X_5$ ), M-point ( $M'_3$ ),  $\Gamma$ -point( $\Gamma_{15}$ ) correspondently. The instability at  $\Gamma$ -point is of the ferroelectric type: in the  $\Gamma_{15}$  mode oxygen ions move



**Figure 2.** a) Calculated phonon spectrum of  $\text{Na}_3\text{OCl}$ , b) calculated phonon spectrum of  $\text{Na}_3\text{OBr}$ . (Imaginary frequencies are indicated by negative values.)

parallel to one of K—O bonds and potassium octahedra move in the opposite direction.

We have performed calculations of the lattice dynamics of the cubic antiperovskite structure of compounds  $\text{A}_3\text{OX}$ . The calculations are based on the DFT using the generalization of Gordon-Kim approach. We found



**Figure 3.** a) Calculated phonon spectrum of  $K_3OCl$ , b) calculated phonon spectrum of  $K_3OBr$ . (Imaginary frequencies are indicated by negative values.)

that these compounds show the same tendency toward distortion as normal perovskites. This conclusion needs in the experimental check.

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**TABLE II** Calculated mode frequencies at a point  $\Gamma(0,0,0)$ .  $\text{cm}^{-1}$  unit is used.

	$\text{Na}_3\text{OCl}$	$\text{Na}_3\text{OBr}$	$\text{K}_3\text{OCl}$	$\text{K}_3\text{OBr}$
$\Gamma_{25}$	75.4	94.9	42.4	54.7
$\Gamma_{15}(\text{LO})$	102.4	87.1	40.6	43.4
$\Gamma_{15}(\text{TO})$	73.8	76.3	178.4i	196.0i
$\Gamma_{15}(\text{LO})$	219.4	216.1	129.2	126.9
$\Gamma_{15}(\text{TO})$	191.4	193.0	57.0	54.6
$\Gamma_{15}(\text{LO})$	381.4	361.2	268.2	252.4
$\Gamma_{15}(\text{TO})$	307.4	281.7	129.3	127.5

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