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First-principles calculations of ferroelectric properties in AA′BB′O$_6$ double perovskites with different types of cation ordering

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First-principles calculations of lattice dynamics and polarization properties have been performed for double perovskite ABiBNbO$_6$ (A – alkali metal Na, Rb, and B – trivalent metal Sc, Lu). Three possible types of A- and B-site cation ordering are studied: layer and columnar ordering of A-site cations with rocksalt ordering of B-site cations, and layer ordering of both cations. The ground state of all compounds is polar with a large value of polarization for all types of cation ordering. For some compounds we obtain spontaneous polarization of 0.7–1.0 C m^{-2} that is twice the BaTiO$_3$ value. For RbBiScNbO$_6$ the lowest-energy state has layer ordering of both A- and B-site cations, which is rare for compounds with double-perovskite structure.

1 Introduction Compounds with the perovskite structure belong to a class of functional materials due to a wide variety of their properties. Ferroelectric and other properties of such compounds change widely depending on their structure and composition [1–11]. Recent development of new technologies of crystals and film growth results in a growing interest in new perspective materials. One of the areas of such interest is a search for new materials with ferroelectric, piezoelectric, and magnetoelectric properties. Different technical applications require compounds with large polarization and piezoelectric coefficients, for example. One of the most prospective materials with such properties are perovskite-like compounds, in particular double perovskites.

In addition, these crystals offer a rich playground from a fundamental physics point of view. Presently, studies of magnetoelectric properties or, for example, rotation of polarization vector on morphotropic boundary or in mixed crystals are attracting particular attention due to the potential for advanced device applications. These and other properties can be found in various compounds with the double-perovskite structure AA′BB′O$_6$. There are a lot of experimental [1–5] and theoretical [6–11] works devoted to the study of double-perovskite properties. Compounds with general formula A$_2$BB′O$_6$, where B and B′ cations have

rocksalt ordering, are well known. However, simultaneous ordering of the cations A, A′ and B, B′ with four different ions can lead to new interesting and useful properties. Such series of double perovskites (ABiScNbO$_6$ (A = Na, K, Rb); SrBiZnNbO$_6$, SrBiMgNbO$_6$, PbBiZnNbO$_6$) were considered and the influence of A or B cations size on ferroelectric properties was studied in [8, 9] (in particular, the effective Born charges and polarization in rhombohedra phase were calculated). Compounds with large spontaneous polarization were predicted in [7] based on unstable phonon modes eigenvectors and energy landscape calculations. Lattice dynamics and the energy of different phases related to rotation of oxygen octahedra were calculated for a number of well-ordered double perovskites ABiBNbO$_6$ (A – alkali metal Na, K, Rb, and B – trivalent metal Sc, Ga, In, Lu) in [11] in the framework of the polarizable-ion model and it was shown that spontaneous polarization may appear in some low-symmetry phases as a secondary effect.

It should be noted that in all the papers mentioned above both A and B cations were considered as ordered in a rocksalt structure. However, as it is known from experiment [6] the sublattice of B-site cations really has rocksalt ordering in general, but such ordering is not typical for the A-site cation sublattice and is not observed experimentally, while normally A cations are ordered in layers. For example, this

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type of ordering was found in a $NaLaMnWO_6$ crystal [10]. In a low-temperature phase this crystal is monoclinic with $P2_1$ symmetry, Na and La ions are ordered in layers and Mn and W ions are ordered in a rocksalt structure. It was shown in [10–12] that additional ordering of A-site cations leads to the appearance of improper ferroelectricity induced by oxygen octahedra rotations.

In the present work the study of double perovskite with the general formula $ABiBNbO_6$, where A – alkali metal Na, K, Rb, B – trivalent metal Sc, Ga, In, Lu started in [11] is continued. Other types of possible ordering of A, A' and B, B' cations has been considered for four compounds from this series when A = Na, Rb and B = Sc, Lu. The aims of this work were simulation and investigation of structure and energy behavior of low-symmetry phases with antiferrodistortive and polar distortions, calculation of spontaneous polarization in the obtained low-symmetry phases for four types of A and B cations ordering. Calculation of full energies and lattice dynamics for all structures was carried out within the density functional theory using the VASP package.

2 Results and discussions
2.1 Cation ordering types in double perovskites
There are three possible patterns of ordering for either the A- or B-site cations in double perovskites. These three types of ordering correspond to interleaving planes of different cations along the crystallographic directions in the perovskite unit cell: along 001 (L), 110 (C), and 111 (R), respectively. Simultaneous ordering of the A and B cations results in nine possible types of ordered structures. For full energy

calculations of ordered structures when A- and B-cations ordered in rocksalt structure (RR) a fcc-lattice was used with one formula unit per unit cell. In the case of double-layer ordering (LL) a tetragonal lattice ($a \times a \times 2a$) with one formula unit per unit cell was used and for other ordering types tetragonal lattice $\sqrt{2}a \times \sqrt{2}a \times 2a$ (a – lattice parameter of perovskite simple cubic cell) with two formula units per unit cell was used.

Energies of completely ordered structures were calculated using the VASP package and Projector Augmented Wave (PAW) pseudopotentials in the framework of density functional theory [13, 14]. A plane-wave cutoff of 400 eV is applied. The Perdew–Burke–Ernzerhof (PBE) was employed for the exchange-correlation potential. The Brillouin zone of the 10-atom fcc cell is sampled by $6 \times 6 \times 6$ Monkhorst–Pack k-point mesh, while that for the 20-atom unit cell is $6 \times 6 \times 4$. Energy differences between a low-symmetry and high-symmetry structures are always computed using an identical k-point mesh. Volume and cell shape were relaxed as well as atomic coordinates until force on the ions would be $<$2–3 meV/Å.

The results of energies and equilibrium lattice parameters calculations for the ordered structures mentioned above are given in Table 1. As can be seen from Table 1, a structure with layer ordering of A- and B-site cations (LL-ordering) is the most favorable. It should be noted that such an ordering type is very rare in double perovskites [6]. The structure with layer-ordered A-site cations and rocksalt-ordered B-site cations is the next favorable. Such (LR) type of ordering is the most common for double perovskites [6, 10]. We must note that LL ordering becomes favorable only after

Table 1 Energies (eV/formula unit) and cell parameters (Å) of high-symmetry structures at different types of cation ordering. The most favorable energies are shown with bold font.

|	type of order		$NaBiScNbO_6$	$NaBiLuNbO_6$	$RbBiScNbO_6$	$RbBiLuNbO_6$
	A	B				
$R3m$	R	R	−73.68	−70.86	−73.98	−70.42
			$a = 4.02$	$a = 4.09$	$a = 4.08$	$a = 4.13$
$P4/mmn$	L		−74.40	−72.06	−74.20	−71.86
			$a = 5.68, c = 8.11$	$a = 5.77, c = 8.28$	$a = 5.74, c = 8.12$	$a = 5.87, c = 8.32$
$P4_2/mmc$	C		−74.06	−71.60	−73.76	−71.48
			$a = 5.71, c = 8.00$	$a = 5.84, c = 8.19$	$a = 5.79, c = 8.03$	$a = 5.90, c = 8.20$
$P4/mmn$	R	L	−73.9	−71.00	−73.42	−70.58
			$a = 5.69, c = 8.07$	$a = 5.84, c = 8.23$	$a = 5.75, c = 8.17$	$a = 5.89, c = 8.31$
$P4mm$	L		**−74.78**	**−72.54**	**−74.36**	**−72.08**
			$a = 3.99, c = 8.28$	$a = 4.03, c = 8.58$	$a = 4.06, c = 8.21$	$a = 4.11, c = 8.45$
$P4/mmm$	C		−74.32	−71.60	−74.04	−71.42
			$a = 5.71, c = 8.09$	$a = 5.86, c = 8.25$	$a = 5.78, c = 8.11$	$a = 5.92, c = 8.26$
$P4_2/mmc$	R	C	−73.54	−70.92	−73.00	−70.62
			$a = 5.68, c = 8.07$	$a = 5.80, c = 8.29$	$a = 5.75, c = 8.15$	$a = 5.86, c = 8.35$
$P4/mmm$	L		−74.10	−71.64	−73.84	−71.52
			$a = 5.66, c = 8.12$	$a = 5.75, c = 8.36$	$a = 5.75, c = 8.11$	$a = 5.84, c = 8.35$
$Pmmm$	C		−73.98	−71.20	−73.58	−71.20
			$a = 5.75, b = 5.70, c = 8.04$	$a = 5.91, b = 5.74, c = 8.23$	$a = 5.84, b = 5.75, c = 8.06$	$a = 6.00, b = 5.80, c = 8.27$

Table 2 Comparison of results obtained using the VASP package and within the polarizable-ion model (GK). The values of effective Born charges Z are given in e units (ω_{FE} – frequency of ferroelectric mode, ω_{AFD} – frequency of mode, related to rotation of oxygen octahedra).

|	NaBiScNbO$_6$		NaBiLuNbO$_6$		RbBiScNbO$_6$		RbBiLuNbO$_6$	
	GK	VASP	GK	VASP	GK	VASP	GK	VASP
a, Å	3.91	4.02	4.07	4.09	3.96	4.08	4.10	4.13
$Z_{Na/Rb}$	1.20	1.15	1.19	1.17	1.28	1.16	1.22	1.17
Z_{Bi}	4.32	6.39	4.01	6.57	4.46	6.55	4.14	6.70
$Z_{Sc/Lu}$	5.66	5.05	1.37	4.61	5.48	5.16	1.76	4.72
Z_{Nb}	6.95	7.21	5.35	7.38	6.78	7.13	5.38	7.21
$Z_{O\parallel}$	−6.23	−5.19	−2.32	−5.09	−6.11	−5.14	−2.54	−4.97
$Z_{O\perp}$	−1.42	−2.35	−1.85	−2.39	−1.44	−2.42	−1.86	−2.46
ω_{FE}, cm^{-1}	−132	−187	−133	−204	−136	−183	−132	−193
ω_{AFD}, cm^{-1}	−188	−283	−221	−305	−177	−276	−213	−299

relaxation of free ion coordinates, while LR ordering is more favorable for the ideal unrelaxed structure of all compounds. It should be noted that we know about the synthesis of only the NaBiScNbO$_6$ compound [15] from the compounds studied here. The structure of NaBiScNbO$_6$ was refined in space group *Pnma* with lattice parameters $a = 5.63$ Å, $b = 7.96$ Å, $c = 5.61$ Å.

Ordering of *B*-cations along [111] direction (R) is known to be the most common. Therefore, in a later part of the work, besides the most energetically favorable structures with double-layered ordering (LL), we consider a different ordering of the cations, keeping B-site cations rocksalt ordered. In [11] calculation of the structures with rocksalt-ordered *A* and *B* cations was performed using Gordon–Kim model. In Table 2 we compare values of lattice parameters, effective Born charges and unstable mode frequencies calculated using a polarizable ion model and VASP package. As can be seen from Table 2 these results have only small quantitative differences. All compounds under consideration are dielectrics, as can be seen from Fig. 1, showing the electronic density of states of RbBiScNbO$_6$ crystal with different types of cation ordering. The electronic density of
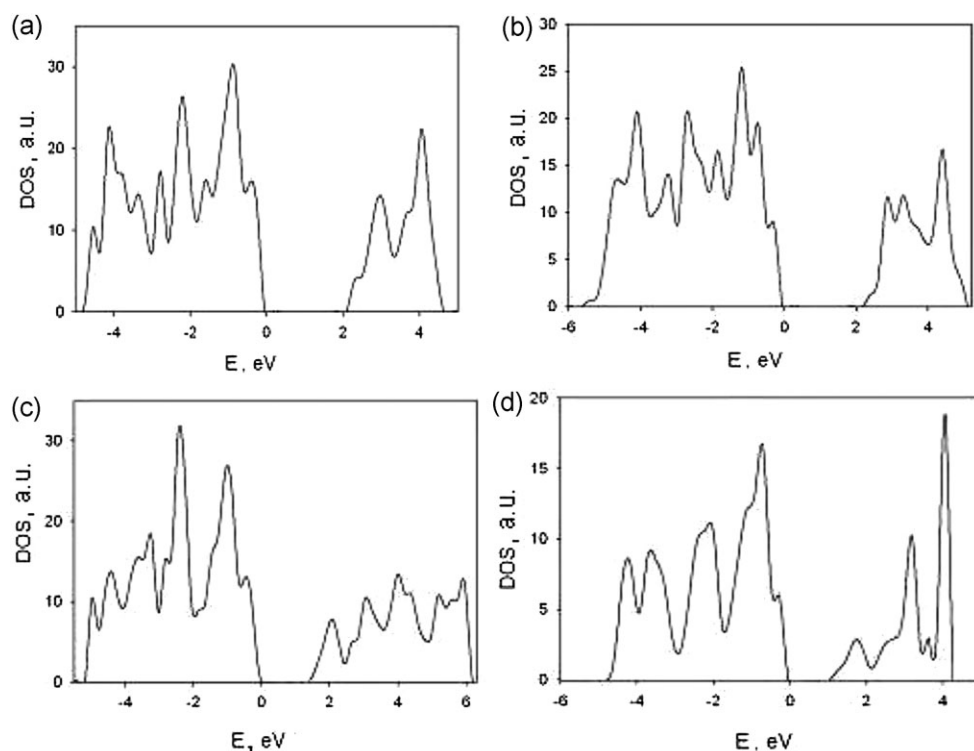
Figure 1 Electronic density of states (DOS) of RbScBiNbO$_6$ for different type of order: (a) Columnar ordering (C) of A-site cations and rocksalt ordering (R) of B-site cations; (b) layered ordering (L) of A-site cations and rocksalt ordering (R) of B-site cations; (c) layered ordering (L) of A-site cations and layered ordering (L) of B-site cations; (d) rocksalt ordering (R) of A-site cations and rocksalt ordering (R) of B-site cations.

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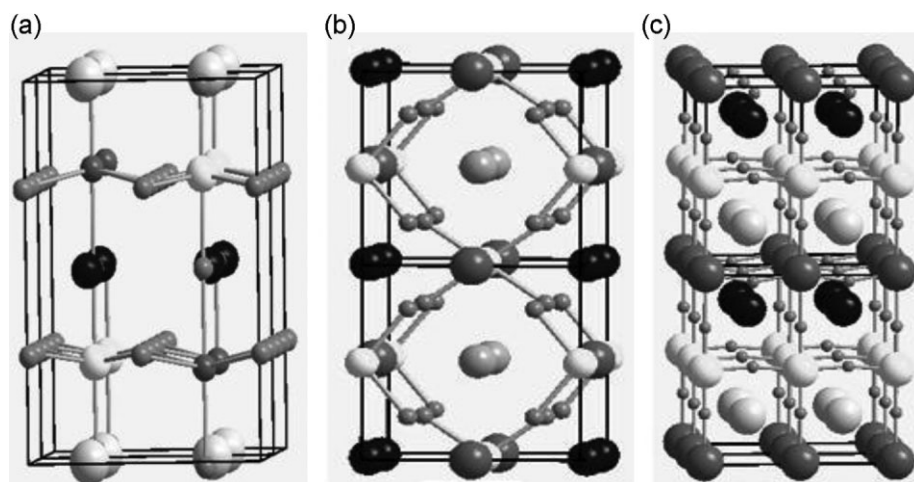
Figure 2 High-symmetry structures for different ordering type: (a) layered ordering (L) of A-site cations and rocksalt ordering (R) of B-site cations; (b) columnar ordering (C) of A-site cations and rocksalt ordering (R) of B-site cations; (c) layered ordering (L) of A-site cations and layered ordering (L) of B-site cations

states has an energy gap of about 2–3 eV (*ab initio* calculations are known to underestimate an energy gap significantly), so it is not surprising that the polarizable-ion model describes the properties of these compounds quite satisfactorily.

In the present work we consider in more detail two other ordering types of *A* cations: layered (L) and columnar (C), keeping B cations ordered in rocksalt structure (R).

2.2 Lattice dynamics of high-symmetry structures Figures 2a–c show high-symmetry structures corresponding to three types of cation ordering for double perovskites. All structures have tetragonal cells, with *P4/mmn*, *P4₂/mm* , and *P4mm* space groups for LR, CR, and LL ordering, respectively. In the case of LR and CR ordering full structure optimization of tetragonal structure leads to small distortion of the oxygen octahedra: all oxygens are clamped to Nb^{5+} ion and oxygen ions O_1 and O_4 (Fig. 3) are shifted to the Bi^{3+} plane. In the case of LL ordering distortions of octahedra with 3-valent and 5-valent cations in center are different: displacements of O_1 oxygen ions to the Bi^{3+} plane are larger than of O_4 ions. In addition, polar *P4mm* symmetry of LL ordering results in ion displacements along the *Z* direction.

All high-symmetry structures with different ordering types are unstable. Decomposition of the vibration representation by irreducible representation for the center of the Brillouin zone can be written as

$$P4/mmn \text{ (LR)}: 6A_{1g} + A_{2g} + 3B_{1g} + 2B_{2g} + 9E_g \\ + A_{1u} + 8A_{2u} + 2B_{2u} + 9E_u,$$

$$P4_2/mmc \text{ (CR)}: 3A_{1g} + 2A_{2g} + 5B_{1g} + 2B_{2g} + 6E_g \\ + A_{1u} + 6A_{2u} + B_{1u} + 4B_{2u} + 12E_u,$$

$$P4mm \text{ (LL)}: \quad 8A_1 + 2B_1 + 10E.$$

Calculated phonon spectra have unstable lattice vibration modes at the center of the Brillouin zone. In the case of LR and CR ordering there are polar unstable modes with E_u (LR), E_u and A_{2u} (CR) symmetry and modes, related to rotations (A_{2g}, A_{1u} and A_{2g}, B_{2g} for LR and CR ordering, respectively) or tilting of NbO_6 octahedra (E_g symmetry). In the case of LL ordering there are only polar unstable modes with *E* symmetry in the center of the Brillouin zone, but unstable modes related to rotations (M_4) and tilting (M_5) of oxygen octahedra belong to a Brillouin zone boundary point M of *P4mm* symmetry group.

2.3 Low-symmetry structures To find stable low-symmetry structures with ordered cations, one or several unstable modes were frozen and full relaxation of the structures was performed. Table 3 shows full energies (per formula unit), lattice parameters and space symmetry groups of the most energetically favorable low-symmetry structures. All the presented low-symmetry structures have no unstable vibration modes.

It was found that the most common ordering type for double-perovskite LR is energetically favorable only for compounds with small cation Na^{1+}. In compounds with Rb^{1+} ions the situation is different: in $RbBiLuNbO_6$ the most favorable is a double-rocksalt ordering (RR), and $RbBiScNbO_6$ double-layered ordering (LL), in the latter compound stable phases for all types of ordering are very close in energy (within 0.05 eV). Using the symmetry mode analysis [10, 16, 17] we decomposed the distortion of the low-symmetry structures into eigenvectors of high-symmetry phase modes. Table 4 shows the amplitudes of these symmetrized distortions and frequencies of the most unstable modes of corresponding symmetry; Fig. 3 shows the ion displacements by eigenvectors of these unstable modes for structures with different ordering types. As one can see from Fig. 3, for all types of ordering instability
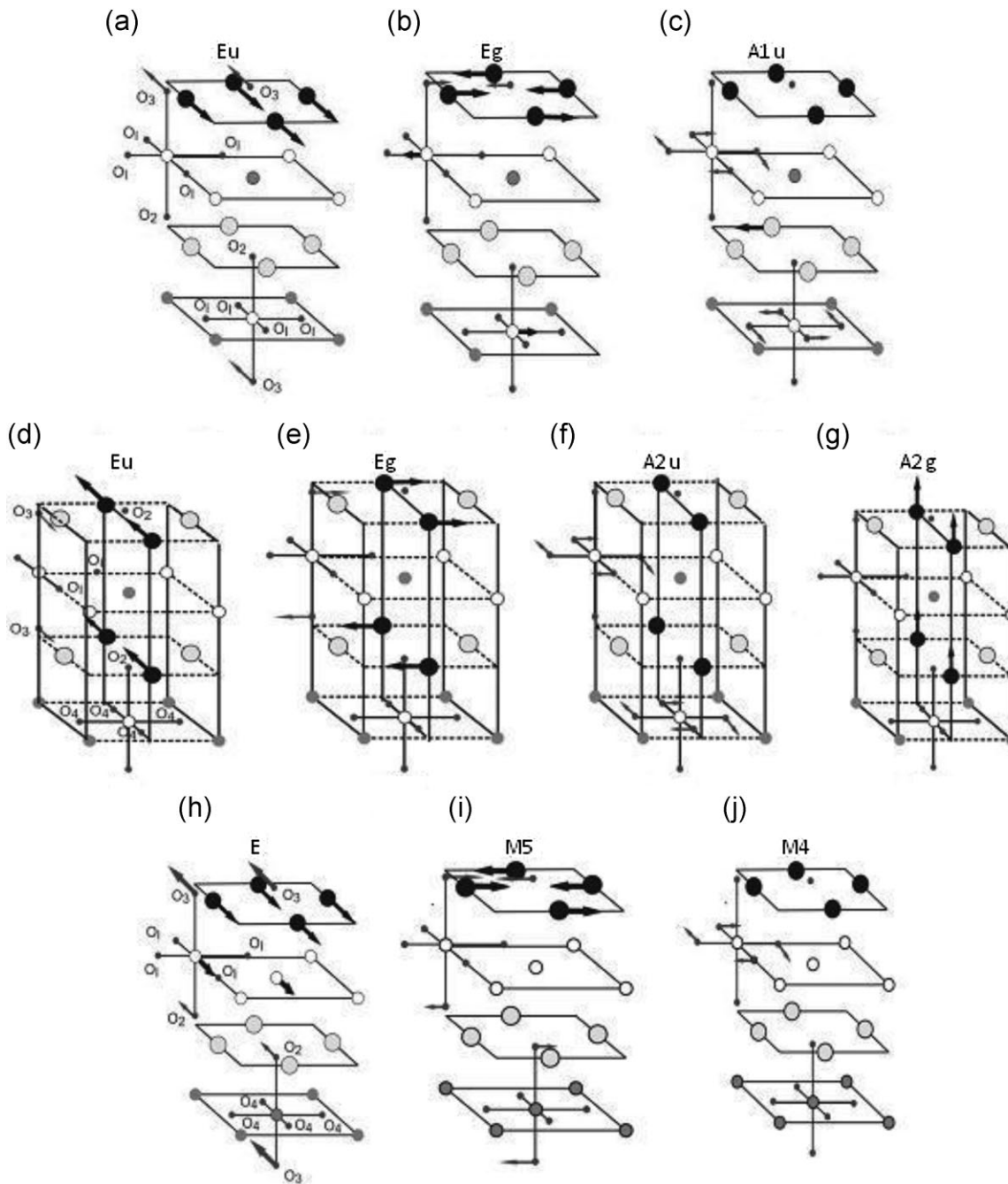
Figure 3 The patterns of ion displacements by unstable modes eigenvector. (a–c): Displacements by E_u, E_g, and A_{1u} modes, respectively, for the structures with layered ordering of A cations and rocksalt ordering of B cations; (d–g): displacements by E_u, E_g, A_{2u} and A_{2g} modes, respectively, for the structures with columnar ordering of A cations and rocksalt ordering of B cations; (h–j): displacements by E, M_5, and M_4 modes, respectively, for the structures with layered ordering of A cations and layered ordering of B cations. Black balls present Bi ions, white balls – B ions, light grey – A ions, dark gray – Nb. Oxygen ions are present by small dark balls.

leading to a stable low-symmetry structure is related to the movements of ions Bi^{3+} and O^{2-} in the plane of Bi$_2$O$_2$ and rotations of NbO$_6$ octahedra. In the case of the A-site cations ordering in the [110] direction (C) $a^0a^0c^+$ rotation (in terms of Glazer notation [18]) is realized, whereas in the case of ordering along the 001 direction (L) structure with $a^0a^0c^-$ rotations is more favorable. The oxygen octahedra rotational

angles φ evaluated from the contribution of the corresponding mode in the resulting distortion are also given in Table 4. It should be noted that in the case of CR ordering two stable low-symmetry structures with close energies were obtained: monoclinic phase $P2$ and triclinic phase $P1$. Monoclinic phase is obtained by freezing one eigenvector component of both twofold modes E_g^x and E_u^y (or E_g^y and E_u^x), following

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Table 3 Energies (eV/formula unit), cell parameters of low-symmetry structures and oxygen octahedron rotational angles (φ) for different types of cation ordering. The most favorable energies are shown with bold font.

type of order	LR	CR	CR	RR	LL
symmetry group	$P2_1$	$P1$	$P2$	$R3$	Pa
NaBiScNbO$_6$	**−75.58**	−75.48	−75.38	−75.32	−75.50
	$a = 5.53$ Å	$a = 5.67$ Å, $\alpha = 89.59°$	$a = 5.69$ Å	$a = 8.00$ Å	$a = 5.66$ Å
	$b = 5.65$ Å	$b = 5.72$ Å, $\beta = 89.95°$	$b = 5.74$ Å		$b = 5.71$ Å
	$c = 8.04$ Å	$c = 7.97$ Å, $\gamma = 90.03°$	$c = 7.86$ Å		$c = 7.99$ Å
	$\beta = 89.79°$		$\beta = 89.80°$		$\beta = 88.58°$
	$\varphi = 12°$	$\varphi = 7°$		$\varphi = 9°$	$\varphi = 12°$
NaBiLuNbO$_6$	**−73.68**	−73.52	−73.50	−73.36	−73.64
	$a = 5.60$ Å	$a = 5.77$ Å, $\alpha = 89.64°$	$a = 5.80$ Å	$a = 8.15$ Å	$a = 5.73$ Å
	$b = 5.75$ Å	$b = 5.84$ Å, $\beta = 90.09°$	$b = 5.86$ Å		$b = 5.79$ Å
	$c = 8.20$ Å	$c = 8.08$ Å, $\gamma = 89.95°$	$c = 8.03$ Å		$c = 8.22$ Å
	$\beta = 89.81°$		$\beta = 90.05°$		$\beta = 88.20°$
	$\varphi = 13°$	$\varphi = 9°$		$\varphi = 10°$	$\varphi = 15°$
RbBiScNbO$_6$	−74.84	−74.43	−74.78	−74.78	**−74.88**
	$a = 5.77$ Å	$a = 5.86$ Å, $\alpha = 90.90°$	$a = 5.83$ Å	$a = 8.26$ Å	$a = 5.79$ Å
	$b = 5.82$ Å	$b = 5.89$ Å, $\beta = 89.81°$	$b = 5.88$ Å		$b = 5.87$ Å
	$c = 8.20$ Å	$c = 8.13$ Å, $\gamma = 90.40°$	$c = 8.13$ Å		$c = 8.20$ Å
	$\beta = 89.82°$		$\beta = 90.54°$		$\beta = 89.63°$
	$\varphi = 3°$	$\varphi = 2°$		$\varphi = 3°$	$\varphi = 6°$
RbBiLuNbO$_6$	−73.08	−72.76	−72.74	**−73.10**	−72.90
	$a = 5.85$ Å	$a = 5.94$ Å, $\alpha = 90.22°$	$a = 5.93$ Å	$a = 8.42$ Å	$a = 5.87$ Å
	$b = 5.90$ Å	$b = 6.02$ Å, $\beta = 89.95°$	$b = 5.99$ Å		$b = 5.95$ Å
	$c = 8.42$ Å	$c = 8.12$ Å, $\gamma = 89.89°$	$c = 8.13$ Å		$c = 8.36$ Å
	$\beta = 89.28°$		$\beta = 89.84°$		$\beta = 89.74°$
	$\varphi = 7°$	$\varphi = 2°$		$\varphi = 4°$	$\varphi = 12°$

Table 4 The unstable mode frequencies (cm^{-1}) in high-symmetry phases and distortion amplitudes (a.u.) by their eigenvector in low-symmetry phases.

		NaBiScNbO$_6$			NaBiLuNbO$_6$			RbBiScNbO$_6$			RbBiLuNbO$_6$		
		ω	distortion amplitude		ω	distortion amplitude		ω	distortion amplitude		ω	distortion amplitude	
Type of order LR ($P4/mmn \rightarrow P2_1$)													
E_g	$P2_1/m$	−220	1.46		−243	1.64		−198	0.61		−205	0.79	
E_u	$Pmn2_1$	−155	0.70		−174	0.73		−154	0.79		−158	0.85	
A_{1u}	$P42_12$	−162	1.18		−227	1.37		−166	0.28		−189	0.72	
Type of order CR ($P4_2/mmc \rightarrow P2, P1$)			P2	P1		P2	P1		P2	P1		P2	P1
E_g	$P2/m$	−289	1.57	1.38	−251	1.76	1.56	−190	0.63	0.49	−219	1.18	0.98
E_u	$Pmm2$	−221	0.74	0.75	−213	0.89	0.86	−194	0.84	0.82	−216	0.96	1.11
A_{2u}	$P4_2mc$	−170		0.24	−173		0.45	−142		0.62	−154		0.31
A_{2g}	$P4_2/m$	−277		0.74	−230		0.91	−155		0.18	−183		0.19
Type of order LL ($P4mm \rightarrow Pa$)													
E	Am	−133	0.85		−148	1.09		−160	0.83		−181	1.00	
M_5	$Pma2$	−148	1.33		−149	1.49		−118	0.38		−123	0.72	
M_4	$P4bm$	−112	0.89		−144	1.11		−112	0.47		−186	0.85	

condensation of any other unstable mode leads to triclinic phase $P1$. All low-symmetry structures appear as a result of condensation of two or more unstable modes, and the magnitude of distortion by different modes depends on the chemical composition of cations. So, in sodium compounds distortion by rotation and tilt modes are larger than the distortion by the polar mode. In rubidium compounds, in contrary, polar distortion increases as the oxygen octahedron rotational angle decreases. This allows us to assume a sequence of phase transitions in the stable low-symmetry

structure. It is most likely that under a temperature decrease, modes with bigger distortion amplitudes would be frozen first: for example, E_g mode in NaBiSc(Lu)NbO$_6$ or E_u mode in RbBiSc(Lu)NbO$_6$. It should be noted that the expansion of the thermodynamic potential in the high-symmetry phases has trilinear invariant coupling distortion by three modes of different symmetries, which are listed below:

$$P4/mmn \ (\text{LR}): \quad \Psi(\eta_x P_y - \eta_y P_x),$$
$$P4_2/mmc \ (\text{CR}): \quad P_z(\eta_x P_x - \eta_y P_y),$$
$$P4mm \ (\text{LL}): \quad \psi(P_y - P_x)(\eta_x - \eta_y).$$

Here, each mode is associated with its own order parameter, namely, twofold modes E_u and E are associated with two-component order parameters (P_x, P_y) and, respectively, E_g and M_4 associated with (η_x, η_y); A_{2u} mode with P_z; A_{1u} and M_5 mode with Ψ. Thus, following condensation of any remaining modes leads to the low-symmetry phase corresponding to the symmetry of cations ordering. In the case of CR ordering distortion corresponding to a rotation of the oxygen octahedrons (A_{2g} mode) in the low-symmetry phase $P1$ is associated with the invariants of the fifth degree:

$$\phi P_y P_x(P_y + P_x)(P_y - P_x),$$
$$\phi \eta_x \eta_y(P_y + P_x)(P_y - P_x),$$
$$\phi P_y P_x(\eta_x + \eta_y)(\eta_x - \eta_y),$$
$$\phi \eta_x \eta_y(\eta_x + \eta_y)(\eta_x - \eta_y),$$

where A_{2g} mode is associated with the order parameter φ.

2.4 Polarization of the low-symmetry structures

Low-symmetry phases are polar for all types of ordering. The polarization P of the various structures can be estimated using the effective Born charges $Z^*_{k,\alpha\beta}$, obtained by *ab initio* calculations, and ions displacement Δu_k from their equilibrium positions in high-symmetry structure with the corresponding type of ordering:

$$P_\alpha = \sum_{k,\beta} Z^*_{k,\alpha\beta} \Delta u_{k,\beta}.$$

Values of the diagonal components of the effective Born charges matrix $Z_{\alpha\alpha}$ and spontaneous polarization are shown in Tables 5 and 6 for one compound as an example. The abnormally large effective charge of Nb^{5+} ion appears for all structures. Note that the Bi^{3+} effective charge, which depends most strongly on the type of cations ordering. Z_{zz} component in the CR type structure is more than twice as large as the nominal charge of bismuth ($+3$), whereas in LR and LL structures such increasing charge value occurs for the Z_{xx} and Z_{yy} components and Z_{zz} component is quite close to the nominal charge. Generally, the values of effective charges only weakly depend on the chemical types of the cations. The difference in their values is noticeable for different types of cation ordering, since, as discussed for example in [19], effective charges in compounds with complex lattice are determined mainly by the structural characteristics, namely, dipole–dipole interactions between cells, which are due to the sublattice position.

On the contrary, the value of spontaneous polarization (Table 6) depends strongly both on the cation composition and ordering type. As can be seen from Table 6, the replacement Na$^{1+} \rightarrow$ Rb^{1+} considerably changes structures of low-symmetry phases: in rubidium compounds rotation and tilting of the oxygen octahedra (E_g, A_{1u}, A_{2g}, M_4 and M_5) is significantly reduced and polar E_u and E distortions become predominant. An especially strong dependence of the spontaneous polarization of the chemical composition was found for LR ordering, where polarization of the sodium-containing compound is almost half as much as of that the rubidium one. As an example we show in Table 6 the value of the polarization for the LR ordering of $Pmn2_1$ structure, obtained by distortion of the high-symmetry $P4/mmn$ structure by one eigenvector component of the most unstable polar mode. As can be seen polarization in low-symmetry $P2_1$ phase of the sodium compounds is almost three times less than in phase $Pmn2_1$, whereas there is not such a strong decrease of polarization in rubidium-containing compounds. This is due to the significant difference in the displacements of the ions in the $P2_1$ phase for NaBiSc(Lu)NbO$_6$ and RbBiSc(Lu)NbO$_6$. So, in sodium compounds, in addition to the displacement of Bi^{3+} and

Table 5 The diagonal components of effective Born charges tensor (in e units) of NaBiLuNbO$_6$ (notation of oxygens corresponds to Fig. 3).

	LR			CR			LL		
	Z_{xx}	Z_{yy}	Z_{zz}	Z_{xx}	Z_{yy}	Z_{zz}	Z_{xx}	Z_{yy}	Z_{zz}
Na	1.22	1.22	1.66	1.36	1.36	1.25	1.14	1.14	1.15
Bi	6.12	6.12	3.26	5.26	5.26	6.39	5.62	5.62	2.83
Lu	4.45	4.45	4.73	5.65	3.39	4.78	3.19	3.19	4.81
Nb	6.95	6.95	6.71	10.38	4.32	7.29	8.92	8.92	6.93
O$_1$	-3.61	-3.61	-1.77	-2.96	-4.11	-2.32	-3.08	-3.08	-1.87
O$_2$	-1.29	-1.29	-6.10	-1.06	-3.31	-5.20	-1.50	-1.50	-5.76
O$_3$	-2.95	-2.95	-3.25	-4.11	-2.95	-2.32	-4.11	-2.95	-2.32
O$_4$				-3.31	-1.06	-5.20	-2.49	-2.49	-3.59

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Table 6 Spontaneous polarization ($C\,m^{-2}$) in low-symmetry phases with different types of cations ordering.

ordering type		LR	LR	CR	CR	RR	LL
symmetry group		$Pmn2_1$	$P2_1$	$P1$	$P2$	$R3$	Pa
NaBiScNbO$_6$	P_x					−0.39	
	P_y	0.87	0.36	0.57	0.50	−0.39	0.68
	P_z			0.34		0.39	−0.30
	$|\boldsymbol{P}|$	0.87	0.36	0.66	0.50	0.67	0.74
NaBiLuNbO$_6$	P_x			0.05		−0.42	
	P_y	0.90	0.33	0.57	0.51	−0.42	0.73
	P_z			0.33		0.42	−0.32
	$|\boldsymbol{P}|$	0.90	0.33	0.66	0.51	0.73	0.80
RbBiScNbO$_6$	P_x			0.20		−0.58	
	P_y	0.76	0.63	0.57	0.58	0.58	0.76
	P_z			0.48		0.58	−0.15
	$|\boldsymbol{P}|$	0.76	0.63	0.77	0.58	1.00	0.77
RbBiLuNbO$_6$	P_x			0.08		−0.58	
	P_y	0.78	0.58	0.61	0.60	0.58	0.78
	P_z			0.14		0.58	−0.17
	$|\boldsymbol{P}|$	0.78	0.58	0.77	0.60	1.00	0.80

corresponding oxygen ions, displacements Na^{1+} ions in the opposite direction to the displacement of Bi^{3+} ions appear (Table 7).

This additional displacement results in the decrease of polarization in the sodium compounds. One of the reasons that these displacements reduce polarization may be as follows. As mentioned above, simultaneous freezing in several unstable modes at the phase transition is hardly probable. We can assume that cooling of the crystal results in freezing of one component of the twofold E_g mode first, since the distortions of this mode in low-symmetry phases are predominant. Phonon spectra of the $P2_1/m$ phase obtained by freezing in only one component E_g mode eigenvector and following relaxation of the structure, show that polar A_u mode remain unstable for all simulated compounds (Table 7). For NaBiLuNbO$_6$ compound eigenvector of A_u mode includes displacements of Na^{1+} ion that are opposite to the displacement of Bi^{3+} ions, while for RbBiScNbO$_6$ such displacements in this mode do not appear. Following condensation of this mode and the relaxation of the structure results in the large displacement of

Na^{1+} and the reduction of polarization in the low-symmetry phase $P2_1$. It should be noted that the phonon spectrum of the high-symmetry $P4/mmn$ phase for sodium compounds includes a second low-energy polar mode ($\omega = -81\,cm^{-1}$) with Na^{1+} and Bi^{3+} ions moving in opposite directions, while in a rubidium compound this mode becomes rigid ($\omega = 124\,cm^{-1}$).

The behavior of the polarization for the CR ordering type is also quite unusual. As shown above, there exist two phases with very similar energies but of different symmetry (monoclinic $P2$ and triclinic $P1$) for this type of ordering (Table 3). However, the directions of the polarization vector in these phases are different: along the Y-axis in the monoclinic $P2$ phase, and along the Z-axis in the triclinic $P1$ one. Such closeness of these energies may result in these phases coexisting.

2.5 Partially ordered structures So our simulation shows that RR and LL ordering types are the most energetically favorable for RbBiLuNbO$_6$ and RbBiScNbO$_6$ compounds, respectively, though rather rare for double

Table 7 Eigenvectors (in arbitrary units) and frequencies (cm^{-1}) of some unstable modes: E_u^s – eigenvector of ferroelectric mode in $P4/mmn$ phase; E_u – polar mode eigenvector in $P4/mmn$ phase; A_u – polar component of unstable mode eigenvector in $P2_1/m$ phase. Δu – vector, corresponding to resulting polar distortion in $P2_1$ phase. (Oxygen notations are given in Fig. 3.)

	NaBiLuNbO$_6$					RbBiScNbO$_6$				
	ω	Na	O$_2$	Bi	O$_3$	ω	Rb	O$_2$	Bi	O$_3$
Δu		−0.22	0.35	0.43	−0.27		0.002	−0.01	0.59	−0.24
E_u^s	−174	0.02	−0.01	0.60	−0.27	−154	0.002	0.01	0.60	−0.27
E_u	−81	−0.55	0.39	0.08	−0.01	124	−0.460	0.23	0.15	0.05
A_u	−116	−0.10	0.09	0.38	−0.33	−66	−0.003	−0.02	0.60	−0.31

perovskites. Compounds of this structural type but with another chemical composition were investigated in a number of studies, and according to experimental data there are successive, but not simultaneous ordering of different cations in this compounds under cooling. Therefore, it is interesting to study partially ordered compounds. Below, we present results of the full energy calculation for these compounds, ordered by only one type of cation. These calculations were performed within the polarizable-ion model [20], because, as was shown above, more complex calculations with the VASP package gives very close results. At the same time, a rough-and-ready model of the polarizable ions is more physically transparent and provides a possibility to compare contributions of different interactions into a total energy of a crystal. To account for disorder of cations AA' and BB' the virtual crystal approximation was used.

Six types of ordered structures were simulated using one lattice parameter a that corresponds to the minimum of the total energy of completely disordered perovskite structure for every composition. For a given cell parameter a coordinates of the ions in partially ordered structures were relaxed to minimize forces at every atom within 1–2 meV/Å. Table 8 shows contributions to the total energy of NaBiScNbO$_6$ and RbBiLuNbO$_6$ crystals, separated according to various interactions.

In all cases the advantage of a particular type of ordering is primarily determined by the Coulomb energy. From electrostatic point of view the rocksalt ordering (R) is the most favorable for B-site cations, then columnar (C) ordering, and a layered ordering type (L) is the least favorable. However, if we take into account other energy contributions (short range and dipole–dipole ones), the picture is different for the compounds with the Sc and Lu ions. In Sc compounds layer ordering becomes more

favorable than columnar ordering. In the case of B-site cation disordering and ordering of A-site cations, from the electrostatic point of view, the most favorable is the structure where the cations AA' have columnar order, but other energy contributions, mainly dipole–dipole ones, lead to an advantage of layered order. But, as can be seen from Table 8, the ordering of the cations BB' is energetically more favorable than the ordering of the cations AA', so ordering of B-site cations in a completely disordered phase (perovskite structure) would be first with the temperature lowered.

3 Summary In summary, we have carried out a first-principles study of lattice dynamics, energy, and polarization behavior of prospective AA'BB'O$_6$ double perovskites with different types of cation ordering (LR, CR, and LL). We find these compounds that are predicted to have ferroelectric instabilities associated with Bi ion displacements have special interest because of their large spontaneous polarization. This fact makes these compounds promising for applications based on the utilization of their polar (ferroelectric) properties.

The most favorable ordering of the high-symmetry phase is a layered structure of both cations. It must be noted that at sequential cation ordering in completely disordered phase, rocksalt ordering of cations BB' turns out to be the most energetically favorable. In fact, most of the existing compounds have layer ordering of AA'-cations and rocksalt ordering of BB'-cations (for example NaLaMgWO$_6$ or NaLaScNbO$_6$ [6, 15]). We note that such ordering takes place in compounds with A = Na^{1+}, but for RbBiScNbO$_6$ compound layered ordering of both cations (LL) with Pa ($Z = 4$) space group turned out to be the most energetically favorable, and rocksalt ordering of both cations (RR) with $R3$ ($Z = 2$) space group for RbBiLuNbO$_6$.

Table 8 Contributions of different interactions into total energy (eV/formula unit) of a crystal for various ordering types of cations (layered ordering (L), rocksalt ordering (R), and columnar ordering (C)), obtained by the polarizable-ion model.

	NaBiScNbO$_6$ 4.02 Å			RbBiLuNbO$_6$ 4.07 Å		
	A-site cations are disordered					
Ordering type of b-site cations	R	C	L	R	C	L
full energy	−8.84	−8.48	−8.72	−14.46	−13.62	−12.24
Coulomb energy	−11.1	−10.40	−10.06	−12.3	−10.88	−9.74
short-range energy	2.9	2.94	2.46	0.92	1.00	1.58
dipole energy	−0.64	−1.02	−1.14	−3.10	−3.74	−3.26
	B-site cations are disordered					
Ordering type of A-site cations	R	C	L	R	C	L
full energy	−6.26	−7.52	−8.06	−6.16	−7.64	−8.36
Coulomb energy	−6.26	−7.14	−5.82	−6.16	−7.18	−6.72
short-range energy	0.00	0.68	0.10	0.00	−0.16	−0.96
dipole energy	0.00	−1.02	−2.34	0.00	−0.28	−0.68

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As is known, it is too hard to realize compounds with LL and RR type of ordering by direct synthesis (compound $NaBiScNbO_6$, synthesized in [15], turns out to be disorder by cations), but we hope that artificial double perovskites with such ordering type can be fabricated. The inclusion of magnetic cations may provide interesting opportunities for the realization of novel multiferroic materials. Therefore, it is necessary to continue to try to get novel ferroelectric materials having interesting and potentially useful physical properties.

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