Structural properties and phase transitions in MgCaSrO quaternary compounds

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ABSTRACT

First-principles calculations of structural properties of MgCaSrO quaternary compounds have been carried out. All possible polymorphs of a certain size (16-atom supercells) are considered in the calculations. The structural phase transitions under pressure in these compounds have been studied, taking into account all possible polymorphs in the competing structures. The details of the phase transition in these compounds were found to be sensitive to the ratio of ionic radii of the constituent alkaline-earth metal atoms. The significant differences at phase transitions of compounds with predominance of Ca atoms from those with predominance of Mg or Sr atoms were found. The cases of predominance of Mg and Sr atoms in these compounds from the point of view of phase transition details, i.e. in the realization through certain polymorphs, coincide completely.

1. Introduction

Quaternary alkaline earth oxides (AEOs) may become in-demand materials in the field of microelectronics in the near future. Despite numerous studies (both experimental and theoretical) of the properties of binary AEOs, only a rather small number of works devoted to ternary AEOs are known at the present time, and the studies carried out for quaternary AEOs are unknown to us at all. The need to study the properties, including quaternary AEOs, changes significantly with reports of the increasing practical importance of ternary oxides which can be used in plasma display panels (PDP). Lee et al. [1] evaluated the possibility of using MgSrO and MgCaO materials for the protective layer instead of the conventional MgO film, and the possibility of using CaSrO as an alternative material in the plasma display panel. Their experimental observations showed that the MgCaO thin film is most promising for high brightness in PDP.

As mentioned above, we know very few works that investigate the properties of ternary oxides. Most of them are devoted to MgCaO alloys. In these works, the study is most often carried out at compositions $x = 0.25, 0.5, 0.75$ and the boundary ones $x = 0$ and 1 for the corresponding binary compounds MgO and CaO. All the following values are calculated depending on the composition of the compound.

Miloua et al. [2] studied the structural parameters (lattice constant a_c and bulk modulus B_0), equation of state $V(p)$, formation energy, and thermodynamic properties ($T - x$ phase diagram) in phase $B1$.

Srivastava et al. [3] reported the structural parameters (lattice constant a_c, bulk modulus B_0 and its derivative B'_0) in phases $B1$ and $B2$, gave the enthalpy-pressure dependence and pressure dependence of phase transitions $B1$–$B2$. Munjal et al. [4] gave the results of calculations of structural parameters (lattice constant a_c, bulk modulus B_0 and its derivative B'_0) and constructed equations of state for ternary compounds in structure $B1$ and for binary compounds in both competing structures. Gulebaglan et al. [5] at composition $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875$ and boundary values $x = 0$ and 1 studied the structure parameter a_c, band gap energy E_g and its bowing parameters for it in the $B1$ lattice. Fan et al. [6] gave the value of the lattice parameter in the $B1$ structure. In addition, elastic constants and elastic moduli, band gap value and calculated band structure and density of state (DOS) were calculated in the $B1$ structure. Almeida-Neto et al. [7] at composition $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875$ and boundary values of $x = 0$ and 1 have studied the enthalpy of formation. The results of calculations of energy band structure for different lattice symmetry and energy gap and density of states are presented. Optical properties (optical absorption coefficient, complex dielectric function) for different lattice symmetry are also considered. Munjal et al. [8] reported the results of calculations of energy band structure, DOS, Compton profile anisotropies, and the equal valence electron density for the $B1$ structure. Stolbov et al. [9] found the dependence of the equilibrium volume as well as formation energies for different structures.

Only a few works known to us are devoted to other ternary oxides.

Table 1
Atomic position for MgCaSrO.

Superlattice type	Atom	Atomic positions
B1-based	Alkaline-earth metal	(0 0 0),
		(1/2 1/2 0),
		(1/2 0 1/4),
		(0 1/2 1/4),
		(0 0 1/2),
		(1/2 1/2 1/2),
		(1/2 0 3/4),
		(0 1/2 3/4)
	Oxygen	(1/2 0 0),
		(0 1/2 0),
		(0 0 1/4),
		(1/2 1/2 1/4),
		(1/2 0 1/2),
		(0 1/2 1/2),
		(0 0 3/4),
		(1/2 1/2 3/4)
B2-based	Alkaline-earth metal	(0 0 0),
		(1/2 1/2 0),
		(1/2 0 1/2),
		(0 1/2 1/2),
		(0 0 1/2),
		(0 1/2 0),
		(1/2 0 0),
		(1/2 1/2 1/2)
	Oxygen	(1/4 1/4 1/4),
		(1/4 3/4 1/4),
		(3/4 1/4 1/4),
		(3/4 3/4 1/4),
		(1/4 1/4 3/4),
		(1/4 3/4 3/4),
		(3/4 1/4 3/4),
		(3/4 3/4 3/4)

Table 2
$A_6B_1C_1O_8$ polymorphs.

Superlattice type	Polymorphs	Example	**Amount**
B1-based	I	AAAAAABC	8
	II	BAAAAAAC	32
	III	AAABAAAC	4
	IV	BAAAACAA	8
	V	BAAACAAA	4
B2-based	A	AAAAAABC	24
	B	AAABAAAC	24
	C	BAAAAAAC	8

Table 3
$A_5B_2C_1O_8$ polymorphs.

Superlattice type	Polymorphs	Example	Amount
B1-based	I	AAAAABBC	32
	II	AAABAABC	8
	III	AABAAABC	8
	IV	BBAAAAAC	16
	V	AAABBAAC	32
	VI	AABABAAC	32
	VII	ABAAABAC	16
	VIII	BAAAABAC	16
	IX	BBAACAAA	8
B2-based	A	AAAAABBC	24
	B	AAABAABC	24
	C	AABAAABC	48
	D	BAAAAABC	24
	E	AABBAAAC	24
	F	BAABAAAC	24

Table 4
$A_4B_3C_1O_8$ polymorphs.

Superlattice type	Polymorphs	Example	Amount
B1-based	I	AAAABBBC	16
	II	AAABABBC	32
	III	AABAABBC	32
	IV	ABAAABBC	16
	V	BAAAABBC	16
	VI	AABBAABC	8
	VII	AAABBBAC	16
	VIII	BBBAAAAC	16
	IX	BAAABBAC	32
	X	AABBBAAC	32
	XI	ABABABAC	16
	XII	BAABABAC	16
	XIII	BABABAAC	16
	XIV	BABAABAC	16
B2-based	A	AAAABBBC	8
	B	AAABABBC	48
	C	ABAAABBC	24
	D	BAAAABBC	24
	E	AABBAABC	48
	F	BAABAABC	24
	G	ABBAAABC	24
	H	BABAAABC	48
	I	ABBBAAAC	8
	J	BBBAAAAC	24

Table 5
$A_4B_2C_2O_8$ polymorphs.

Superlattice type	Polymorphs	Example	Amount
B1-based	I	AAAABBCC	8
	II	AAABABCC	32
	III	BAAABACC	8
	IV	BAAAABCC	8
	V	AABBAACC	4
	VI	AAAABCBC	16
	VII	AAABACBC	32
	VIII	AABAACBC	32
	IX	ABAAACBC	32
	X	BAAAACBC	32
	XI	AABBACAC	32
	XII	ABABACAC	16
	XIII	BAABACAC	32
	XIV	BABAACAC	16
	XV	AAACABBC	32
	XVI	AABCAABC	12
	XVII	AAACBBAC	8
	XVIII	BAACABAC	8
	XIX	ABCAAABC	32
	XX	AACBAABC	4
	XXI	BBCAAAAC	8
	XXII	ABCAABAC	8
	XXIII	BACAABAC	8
B2-based	A	AAAABBCC	12
	B	AAABABCC	48
	C	AABAABCC	24
	D	ABAAABCC	24
	E	AABBAACC	48
	F	BAABAACC	12
	G	ABABACAC	12
	H	AAACABBC	48
	I	AABCAABC	48
	J	BACAABAC	12
	K	AAACBBAC	24
	L	AABCABAC	24
	M	ABACABAC	24
	N	CAAAABBC	24
	O	CABAABAC	12
	P	CBAAABAC	24

Labidi et al. [10] found structural parameters (lattice constant a_c, bulk modulus B_0), gap energy E_g and optical properties (refractive indices, optical dielectric constant) for the compound $Mg_{1-x}Sr_xO$. Srivastava et al. [11] for the same compound, having calculated the lattice constant a_c, bulk modulus B_0 and enthalpy, they found the phase transition pressures p_{pt}. Ghebouli et al. [12] found equilibrium characteristics (lattice constant a_c, bulk modulus B_0) for the compound $Sr_{1-x}Ca_xO$. Band

Table 6

$A_3B_3C_2O_8$ polymorphs.

Superlattice type	Polymorphs	Example	Amount
B1-based	I	AAABBBCC	16
	II	BAAABBCC	16
	III	AABBABCC	16
	IV	ABABABCC	16
	V	BAABABCC	16
	VI	AAABBCBC	32
	VII	BAAABCBC	32
	VIII	AABBACBC	32
	IX	ABABACBC	32
	X	BAABACBC	32
	XI	ABBAACBC	32
	XII	BABAACBC	32
	XIII	BBAAACBC	32
	XIV	ABBBACAC	32
	XV	BABBACAC	32
	XVI	AAACBBBC	16
	XVII	AABCABBC	16
	XVIII	ABACABBC	16
	XIX	BAACABBC	16
	XX	ABACBBAC	16
	XXI	AACABBBC	16
	XXII	AACBABBC	16
	XXIII	ABCAABBC	16
	XXIV	BACAABBC	16
	XXV	ABCABBAC	16
B2-based	A	AAABBBCC	24
	B	AABBABCC	24
	C	AABBABCC	48
	D	ABABABCC	48
	E	BAABABCC	24
	F	ABBAABCC	24
	G	ABBBAACC	24
	H	BABBAACC	24
	I	AAACBBBC	24
	J	AABCABBC	48
	K	ABACABBC	48
	L	BAABABBC	48
	M	ABBCAABC	24
	N	AABCBBAC	48
	O	CAAABBBC	8
	P	CAABABBC	48
	Q	CBAAABBC	24

gap energy and bowing parameter for it are also calculated. In addition, thermodynamic properties, namely, enthalpy of mixing ΔH, capacitances, entropy, Debye temperature and $T - x$ phase diagram are given.

Note also that in our previous paper [13] structural characteristics (lattice constants a_c, bulk moduli B_0 and their pressure derivatives B'_0) were found for ternary oxides. In addition, the results of calculations of phase transition pressures p_{pt} and reduced volumes under phase transition $B1$–$B2$ are carried out. Energy gaps E_g and its dependence on composition in $B1$ and $B2$ phases are also found. All calculations were performed at composition $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875$ and boundary values $x = 0$ and 1 for the $B1$ and $B2$ lattices.

The main purpose of this work is to investigate the structural properties of MgCaSrO quaternary compounds and phase transitions in them.

Already even calculations of ternary compounds can be quite costly. For quaternary compounds the problem is aggravated. In the framework of this work, calculations for all polymorphs of different symmetries with the corresponding supercell size have been carried out. The implementation details of such approach are discussed in the next paragraph.

Other approaches to the calculation of investigated values of multi-component compounds are also known. In some calculations only one of possible polymorphs is investigated. The chosen supercell may coincide with the unit cell. In such calculations, there is a possible loss of information associated with unexamined polymorphs.

The opposite situation occurs in the framework of special quasirandom structures (SQS) of [14,15] calculations, where the supercell under study can be much larger than the unit cell used for calculations, which replaces in some approximation (with some accuracy) the original supercell in the calculations of the characteristics under study.

Approaches that combine known (calculated) information for the corresponding compound with a smaller number of components, up to taking into account the properties of individual atoms in calculating the properties of binary compounds, and further possible prediction of the properties of ternary and even quaternary compounds [16] may also be of some interest. Our approach is more costly but provides more complete information due to the consideration of all polymorphs of the allowed (chosen) size.

This paper is organized as follows. In Section 2, the computation details are described. Next, the structural properties and phase transition characteristics of MgCaSrO alloy are presented in Section 3. Finally, the conclusions are summarized in Section 4.

2. Computational details

Restricting ourselves to a supercell of a certain size, which contains some fixed number of atoms in corresponding positions, we can try to search through all possible combinations of atom arrangements. Naturally, the number of such combinations grows exponentially as the size of the supercell and, correspondingly, the number of atoms in it increases, so it makes sense to limit the consideration to supercells of reasonable size. However, the fact that, due to symmetry, many such combinations represent the same polymorph, i.e., have the same values of thermodynamic quantities, significantly reduces the number of combinations necessary for consideration. Further, for each polymorph only one of all possible combinations of atoms in atomic positions is considered, which considerably reduces the volume of calculations and opens the way to carrying out such calculations at reasonable costs. The AEO's crystallize in the B1-structure at p=0 and undergo the B2-structure transition when the pressure is increased. Supercells of quaternary oxides are obtained by all possible substitutions of atoms of different alkaline-earth metals (in general case different species of metal atoms are denoted hereinafter by literals A, B and C, which allows to take into account the symmetry when they change places) at their corresponding positions in B1- and B2-lattices. The structures obtained in this way are further referred to as B1-based and B2-based, respectively.

A $1 \times 1 \times 2$ supercell was used for the B1-based structures and a $2 \times 2 \times 2$ supercell for the B2-based ones, which both contain 16 atoms each. Half of the lattice positions are occupied by oxygen atoms, and the other half is filled with atoms of alkaline-earth metals. The atomic positions (in terms of the superlattice constant, a_c) in the structures under consideration are listen in Table 1.

It is convenient to use the designation $A_mB_{8-m-n}C_nO_8$ where m and n ($m, n = 1, …, 6$) are the numbers of atoms of the alkaline earth metal species A and C, respectively, along with the designation $A_xB_{1-x-y}C_yO$ (where x and y take values 0.125, 0.25, 0.375, 0.5, 0.625, 0.75). Information about polymorphs of various compounds $A_mB_{8-m-n}C_nO_8$ is presented in the form of tables in which polymorphs of B1-based structures are numbered with Roman numerals, and B2-based ones are denoted by capital Latin letters. In the last column of the tables, the number of structural combinations corresponding to a given polymorph is indicated, one of which is presented as an example in the penultimate column. The order of the atoms in the examples in Table 2 corresponds to the order in which the positions of the atoms are listed in Table 1. Tables show polymorphs of compounds $A_6B_1C_1O_8$ (Table 2), $A_5B_2C_1O_8$ (Table 3), $A_4B_3C_1O_8$ (Table 4), $A_4B_2C_2O_8$ (Table 5), $A_3B_3C_2O_8$ (Table 6).

The first-principles calculations are performed using the Quantum ESPRESSO code [17] with the Vanderbilt pseudopotential [18] for all elements, except for magnesium, for which the Troullier – Martins pseudopotential [19] was applied. The cutoff for the kinetic energy is $E_{cut} = 70$ Ry for the wave function, and 700 Ry for the charge density has been used. The exchange-correlation potential was calculated using Perdew – Burke – Ernzerhof (PBE) parametrization [20]. The Brillouin
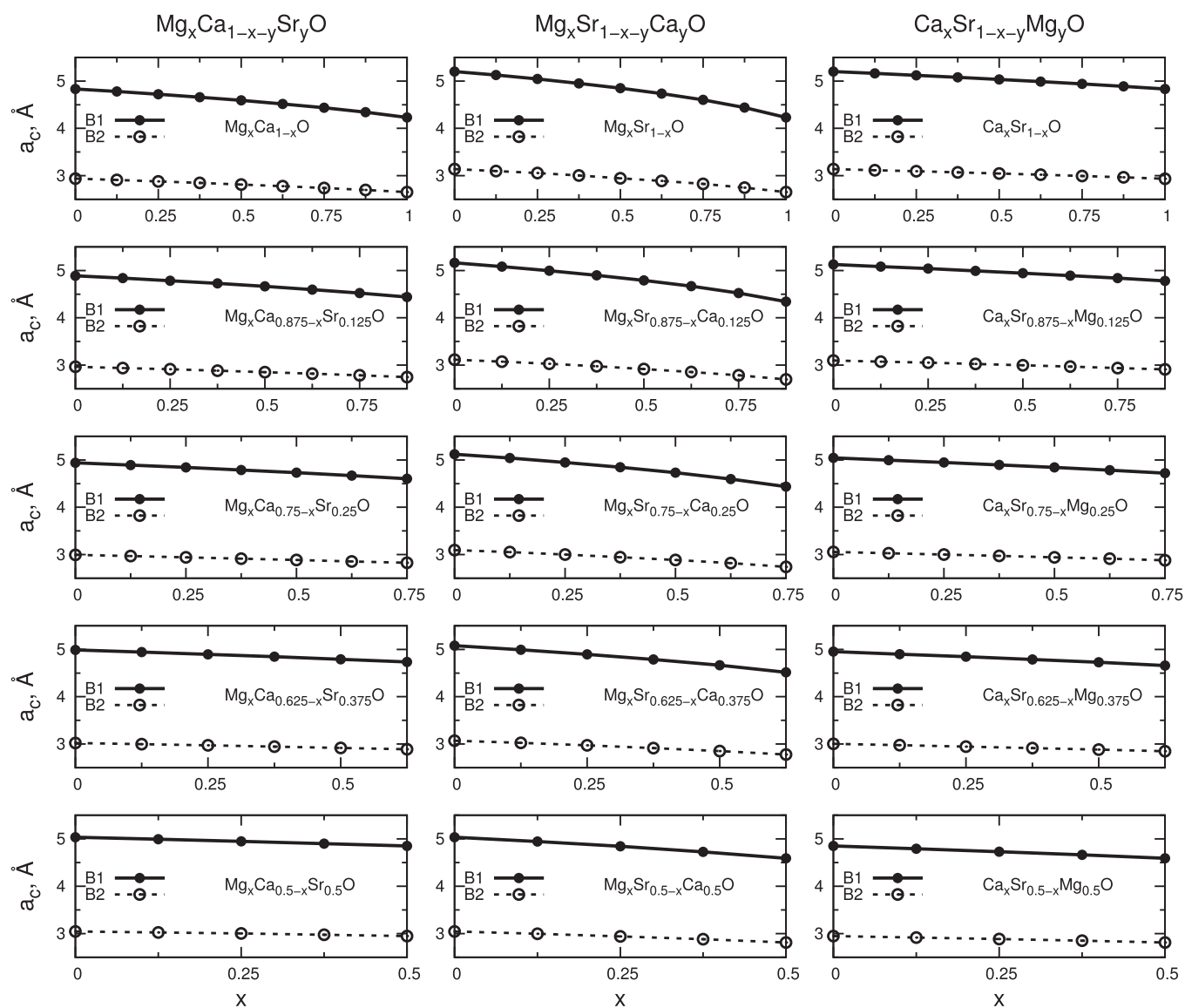
Fig. 1. Equilibrium lattice constants of MgCaSrO as a function of composition in B1- and B2-based superstructures.
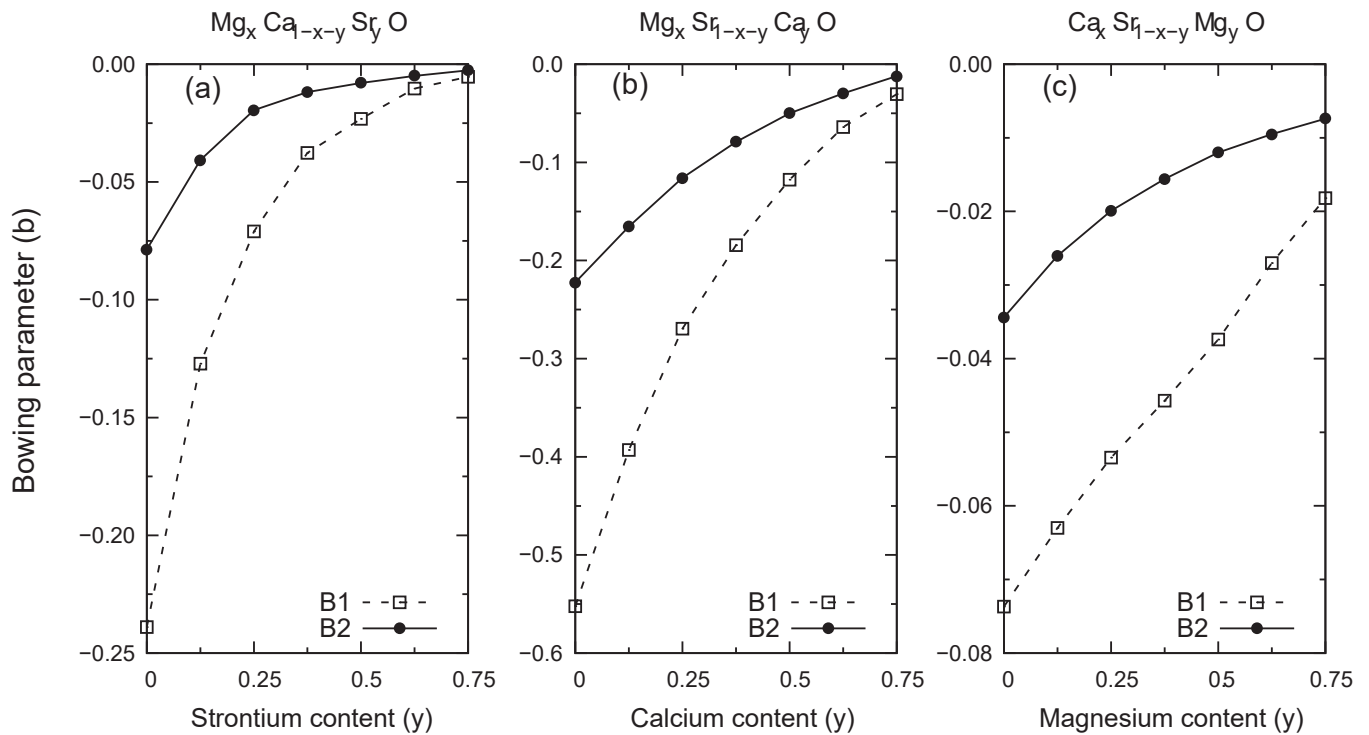
Fig. 2. Composition dependence of the bowing parameter for MgCaSrO quaternary alloys.

zone integration was performed by means of the Monkhorst – Pack method [21] with a $4 \times 4 \times 2$ special k-point mesh of $1 \times 1 \times 2$ B1-based supercell and a $4 \times 4 \times 4$ special k-point mesh of $2 \times 2 \times 2$ B2-based supercell, which is sufficient for accuracy no worse than $1 \cdot 10^{-4}$ Ry.

3. Results and discussions

3.1. Structural properties

The structural properties of $A_x B_{1-x-y} C_y O$ quaternary alloys have been studied by fitting calculated data to the third order Birch – Murnaghan's equation of state [22,23]. As a result of these calculations equilibrium properties of cubic structures of these compounds were found: equilibrium volumes (V_0), superlattice constants (a_c), bulk moduli (B_0) and their pressure derivatives (B'_0) in B1- and B2-based lattices in which cation positions are occupied by alkaline-earth metal atoms as indicated in Table 1.

The dependence of a_c on the composition x and y can be seen in Figure 1.

The value of y varies from 0 to 0.5 from the top row to the bottom row. Such dependences are often close to Vegard's law, which for ternary compounds has the form

$$a_c(A_x B_{1-x}O) = x\, a_c(AO) + (1-x)\, a_c(BO)$$

where $a_c(AO)$ and $a_c(BO)$ are equilibrium lattice constants of AO and BO binary compounds, respectively, $a_c(A_x B_{1-x}O)$ is the superlattice constant of the alloy.

In case of sufficiently strong deviation from the linear Vegard's law, the obtained dependence can be refined through the introduction of bowing parameter, b,

$$a_c(A_x B_{1-x}O) = x\, a_c(AO) + (1-x)\, a_c(BO) - x\,(1-x)\, b.$$

In the case of quaternary $A_x B_{1-x-y} C_y O$ compounds, these formulas apply only when y=0. At $y = const \neq 0$ we use in case of taking into account nonlinearity of dependence the formula

$$a_c(A_x B_{1-x-y} C_y O) = x\, a_c(A_{1-y} C_y O) + (1-x)\, a_c(B_{1-y} C_y O) - x\,(1-x)\, b.$$

Figure 2 shows the results of calculating the bowing parameter as a function of the Sr, Ca and Mg content added to the MgCaO, MgSrO and CaSrO compounds, respectively.

Among these ternary compounds, the highest bowing parameter of -0.55 was found for MgSrO [13]. Figure 2 also shows that the bowing parameter decreases (in absolute value) with increasing content of the third (added) alkaline-earth metal in both B1-based and B2-based compounds, bringing the considered dependence closer to Vegard's law. The noticeably larger bowing parameter in MgSrO and MgCaO containing Mg was explained in [13] by the marked difference of the ionic radius of Mg from the ionic radii of Ca and Sr.

The ionic radii of alkaline-earth metals and their role in binary oxides and chalcogenides are considered in detail in [24], where their pressure dependence was also investigated, but magnesium ions were not studied within the framework of that work. Thus, the bowing parameter of MgSrO with the largest ratio of ionic radii of Sr and Mg (approximately 1.6) is the largest, and the lowest is that of CaSrO with the smallest ratio of ionic radii of Sr and Ca (approximately 1.15).

Figure 3 shows the bulk moduli, B_0, of the quaternary oxides. The composition dependences of B_0 for oxides are very similar in B1- and B2-based structures. As in Figure 1 here y increases from 0 to 0.5 from top to bottom. As y increases, there are minor changes in the mutual arrangement of B1- and B2-based dependences. Figure 3 shows that with increasing addition of Ca atoms to the MgSrO compound (middle column), almost nothing changes in this sense. In contrast, in the last column with increasing Mg in the MgSrO compound, it is quite clear that the dependence of B_0 on the Ca composition in the compound changes from the excess of the corresponding B2-based curve over the B1-based one to the reverse situation at $y = 0.5$, i.e., the B1-based dependence dominates over the B2-based one. Perhaps increasing the Mg content changes the lattice more significantly than when Ca and Sr are added.
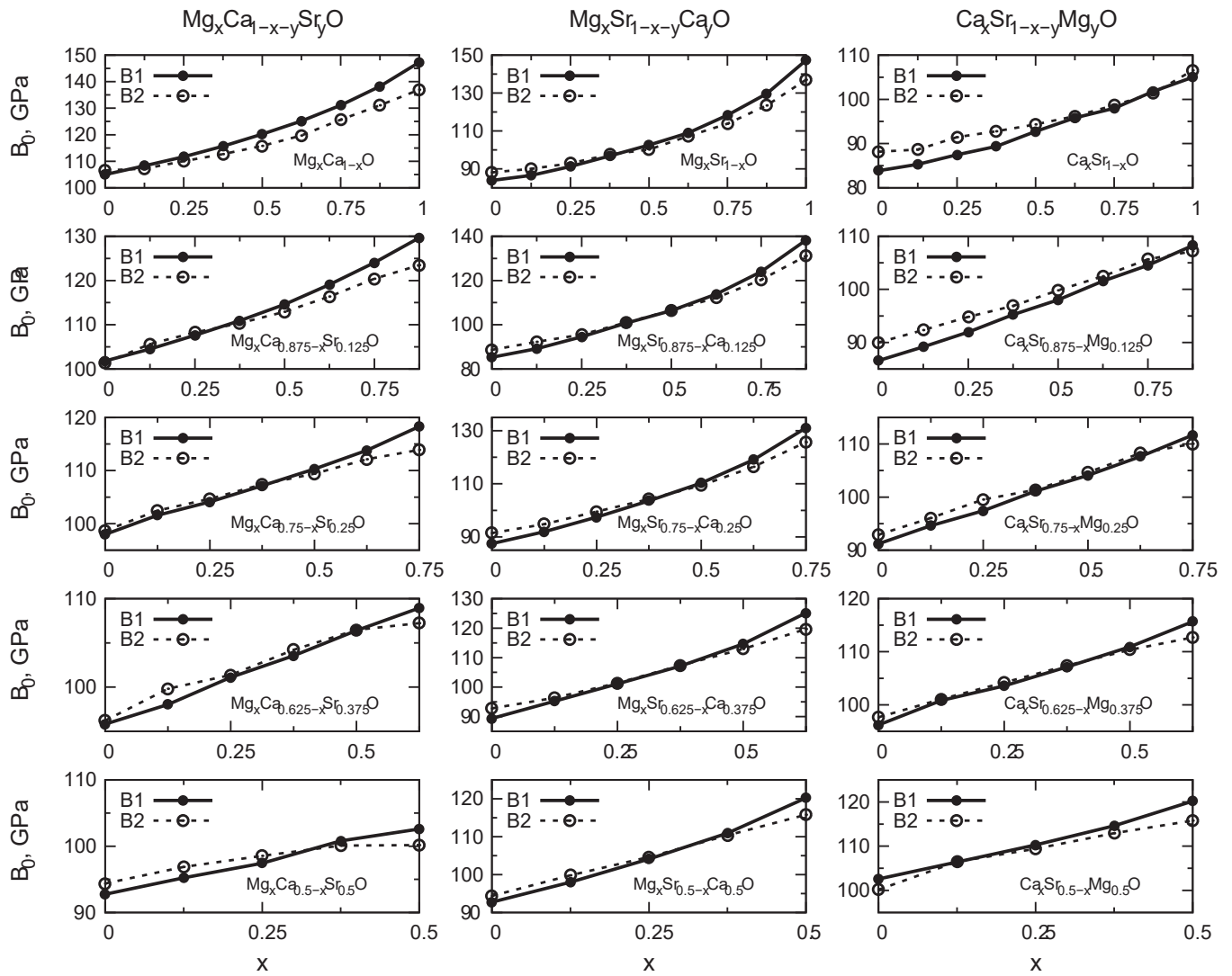
Fig. 3. Bulk moduli of MgCaSrO as a function of composition in B1- and B2-based superstructures.
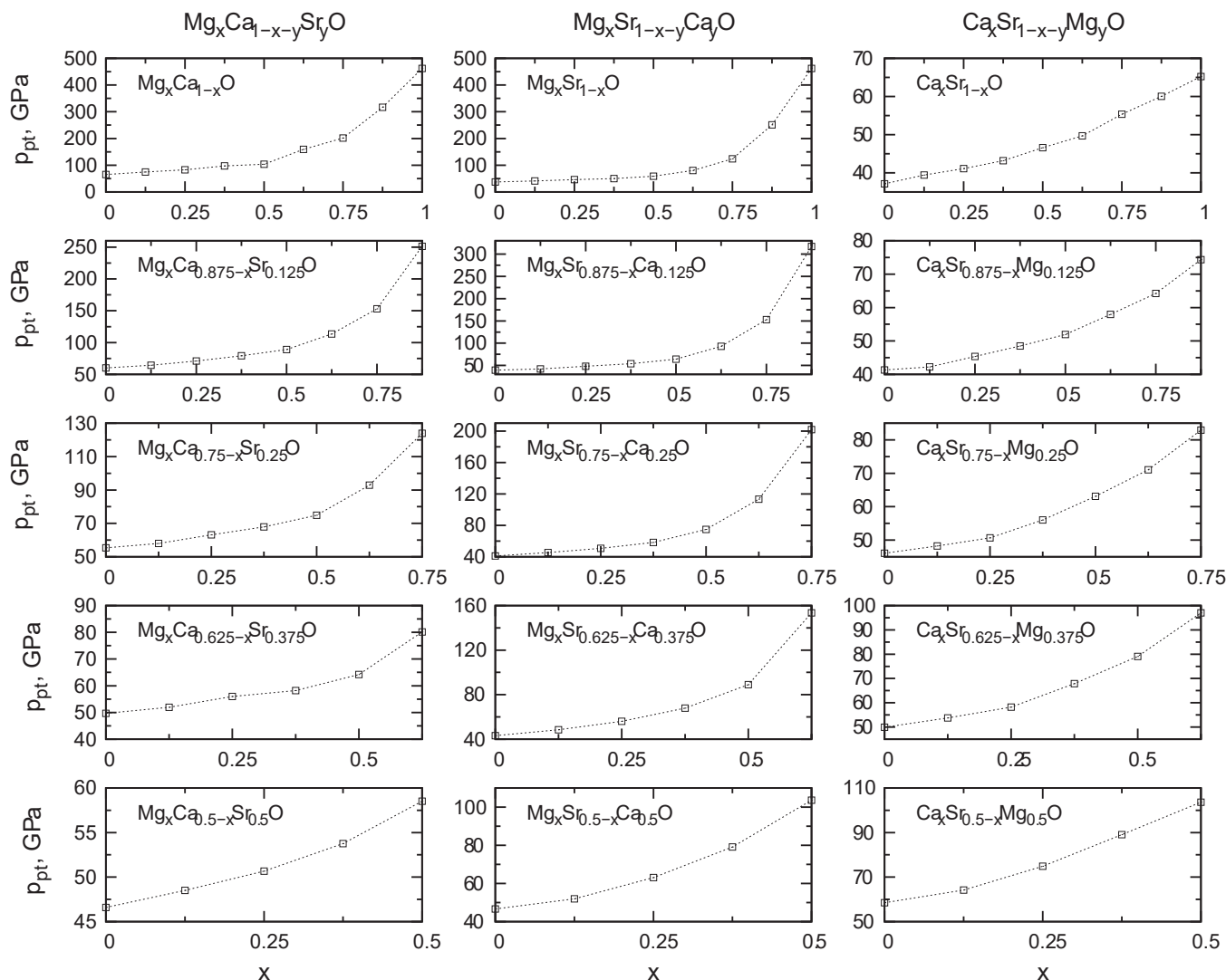
Fig. 4. Phase transition pressures in MgCaSrO as a function of composition in B1- and B2-based superstructures.

Table 7

Accuracy of first-principles calculations in binary compounds compared to experiment (in %).

Compound	$a_c(B1)$	$B_0(B1)$	$p_{pt}(B1 \rightarrow B2)$
MgO	0.5	5.6	—
CaO	0.5	5.6	3.6
SrO	0.8	8.1	3.2

3.2. Phase transition characteristics

The main purpose of this paper is to study the phase transitions under pressure from B1- to B2-based structure in MgCaSrO quaternary compounds. Before this, similar phase transitions in ternary oxides MgCaO, MgSrO, CaSrO have been studied in detail [13].

The standard approach of calculating and comparing enthalpies of competing structures is used to investigate phase transitions. Using the third-order Birch - Murnaghan's equation of state [22,23] one can find the equilibrium values of the total energy E, the volume V, the bulk modulus B_0 and its pressure derivative B'_0 by least-squares fit of calculated $V - E$ curves. Comparison of the energies of all possible polymorphs realizing given superstructure allows us to find the most energetically advantageous polymorphs for both B1-based and B2-based superstructures.

Then, passing to the $p - V$ form of the third-order Birch - Murnaghan's equation of state, we find the pressure values with volume change and the corresponding enthalpy ($H = E + pV$) of the competing phases (polymorphs or, if necessary, superstructures).

It turned out that when all possible polymorphs are considered, even and very limited supercell size, phase transitions between different polymorphs of the same compound sometimes appear. In this case, of course, different variants are possible, since the phase transition pressure between polymorphs can be either greater or less than the phase transition pressure between the different phases of a given compound. In this work, only one such transition in Ca$_{0.75}$Mg$_{0.125}$Sr$_{0.125}$O is found for quaternary MgCaSrO compounds. Interestingly, for ternary compounds, a similar phase transition was found in Ca$_{0.75}$Sr$_{0.25}$O [13], very similar to the one found here. As for the compound Ca$_{0.75}$Mg$_{0.125}$Sr$_{0.125}$O, in it, the transition between polymorphs I - V occurs at $p = 28.62$ GPa and only then the B1 – B2 transition occurs, namely, the V - C transition at $p_{pt} = 64.24$ GPa. It may also be interesting that in the B1-based phase there is another transition between polymorphs at increasing pressure, namely V - III at $p = 115.6$ GPa, which is not observed in the other studied compounds.

Phase transition pressures as a function on composition x are represented in Figure 4, where, as in Figures 1 and Figures 3, y grows from 0 to 0.5 from top to bottom.

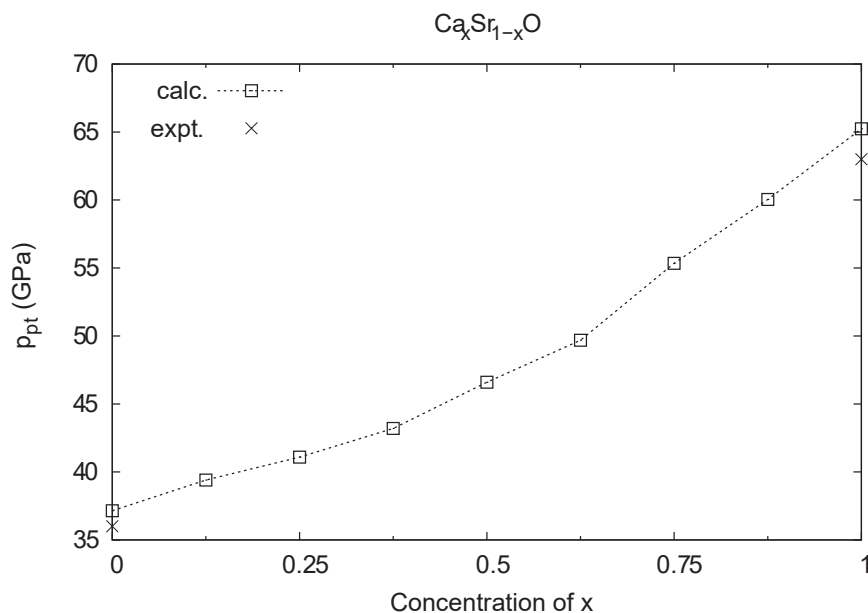In order to try to determine the accuracy of the presented first-

Fig. 5. Illustration of the accuracy of first-principles calculations using the example of phase transition pressure values.

principles calculations of quaternary oxides, it should be recalled that experimental data are available only for binary oxides. The rather high accuracy of calculations of this kind in computing lattice parameters, which is usually less than 1 %, is well known. However, it should be noted that the results for bulk modules are usually an order of magnitude worse. That is, Table 7 reflects well the usual accuracy of calculations within the framework of density functional theory. Of course, for binary compounds of this kind these calculations at insignificant expenditure of resources are carried out on the basis of consideration of a unit cell of very small size, which allows us to sufficiently increase the calculation parameters (cutting energy, number of special points in the Brillouin zone).

As for phase transition pressures, the results of first-principles calculations can be even worse, for example in metals. However, in compounds with a sufficiently large band gap, which are AEO's, the accuracy of determining the phase transition parameters is much higher. Table 7 shows that it is of the order of 3 %.

To consider the results of the ternary compounds calculations we turn to Figure 5. It is convenient for this purpose to consider compounds based on CaO and SrO, since for MgO there is no confirmation of calculated values of phase transition pressures, which exceed the possibilities of experiment at the moment (about 450 GPa and higher). Figure 5 shows the dependence of the phase transition pressure, p_{pt}, on the Ca content in the ternary oxide $Ca_xSr_{1-x}O$. Known experimental values for CaO and SrO are represented by crosses. It is very likely that the calculated values, as perhaps the imaginary curve constructed from them, run higher, as do the values calculated for the binary oxides themselves. Therefore, it is likely Figure 5 represents about the same accuracy of the calculated values for ternary oxides. In contrast to the calculations of binary oxides [13], the ternary compounds whose results are used for Figure 5 [24] were calculated with the same parameters as the quaternary ones considered here. Therefore, there is no reason to believe that the accuracies of these calculations differ markedly from each other.

We visualize the results of calculations of phase transition pressures using ternary diagrams. Figure 6 shows the structural symmetry of quaternary oxides in B1- and B2-based lattices. Structurally identical compounds, which differ only by rearrangement of Mg - Ca - Sr atoms in the corresponding atomic positions, are labeled with the same geometric figure. For example, $A_{0.75}B_{0.125}C_{0.125}O$ compounds are represented by circles, $A_{0.625}B_{0.25}C_{0.125}O$ compounds by squares, etc. To the right of

these geometric signs is the number of polymorphs for a given structure (number on top for B1-based structure, number on the bottom for B2 one). For comparison, on the left border of the diagram, the same information is given for ternary compounds.

Figure 7 shows the results of the search for phase transitions between the polymorphs of each quaternary compound. Polymorphs with the lowest total energy are indicated near the point corresponding to a certain compound (above the point for B1-based structure, below the point for B2 one). Comparing Figures 6 and Figures 7, we find a loss of symmetry in the lower left corner, which corresponds to quaternary CaO-based compounds. In the other two corners, the presence of symmetry only slightly different from that of Figure 6 is readily apparent. This also finds its explanation in terms of the values of ionic radii of alkaline-earth metals. In the upper corner of the diagram, only atoms (Ca and Sr) with larger ionic radii are added to the MgO compound, resulting in lattice broadening effects and an increase in the lattice constant. Similarly, in the right corner of the diagram, only atoms (Mg and Ca) with smaller ionic radii are added to the SrO compound, resulting in lattice contraction effects and a decrease in the lattice constant. These phenomena appear to be similar in terms of symmetry. However, for CaO we have a different case, since the addition of atoms with both smaller and larger ionic radii occurs, which most likely leads to all sorts of lattice deformations and affects the values of thermodynamic quantities, including the total energies of polymorphisms of the corresponding compounds. Using the data partially presented in Figure 4, we can consider the dependences of phase transition pressures on composition, from which we obtain the final ternary diagram of phase transitions for MgCaSrO (Figure 8).

4. Conclusions

First-principle calculations of MgCaSrO quaternary compounds have been performed in order to study the structural properties of these compounds under pressure and phase transitions in them.

It was found that the properties of these compounds are sensitive to the ratio of ionic radii of their constituent alkaline-earth metal atoms. Since the largest differences in ionic radii are inherent in the Mg - Sr pair, the largest bowing of the dependence of structural properties on composition, i.e. a noticeable deviation from Vegard law (Figure 2(b)), is observed at low content of Ca atoms, and the smallest is observed at low content of Mg atoms (Figure 2(c)). The bulk modulus B_0 in the B1-
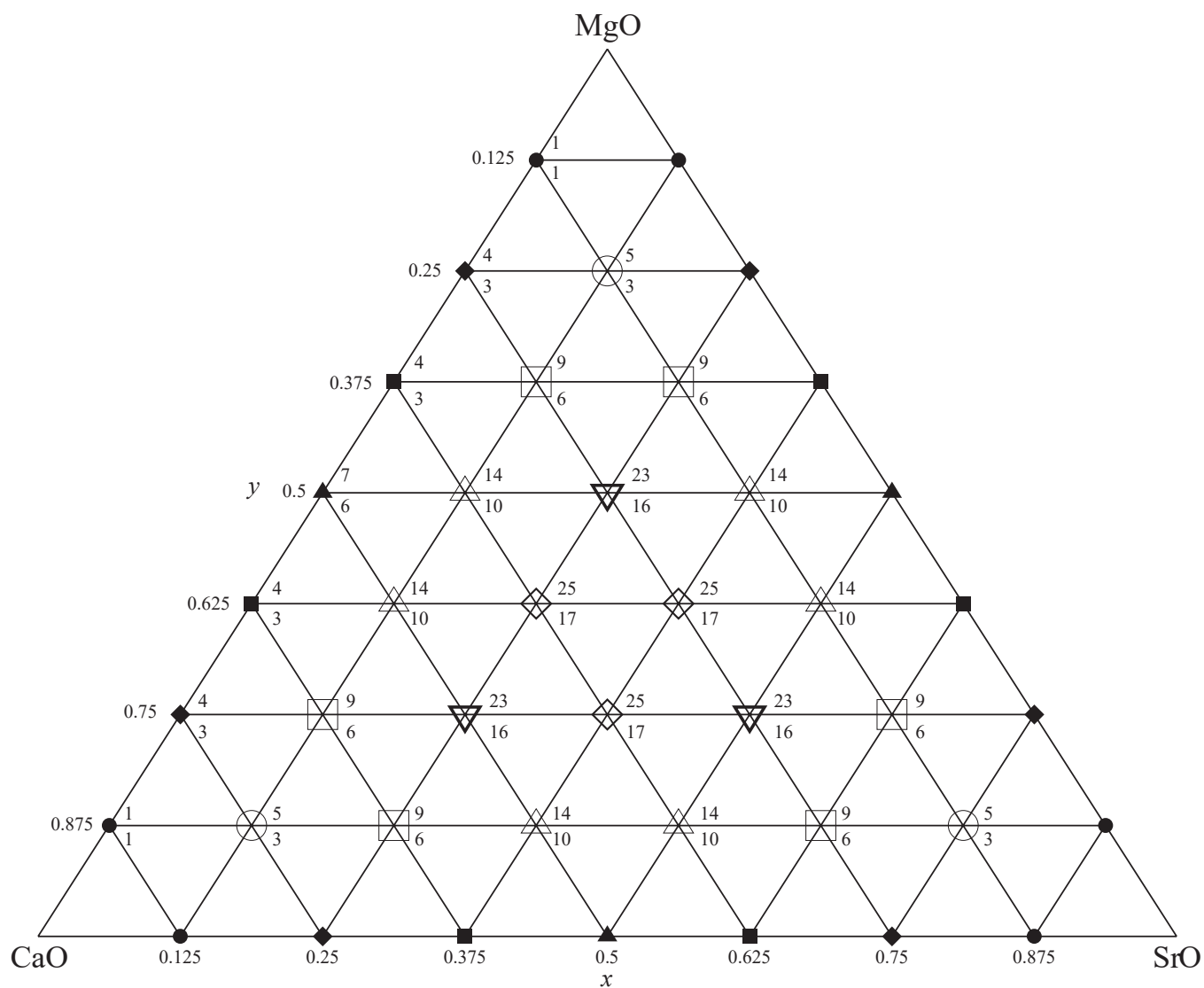
Fig. 6. Number of polymorphs in compounds $Mg_{1-y}Ca_{1-x}Sr_{x+y-1}O$ in $B1$- and $B2$-like structures.
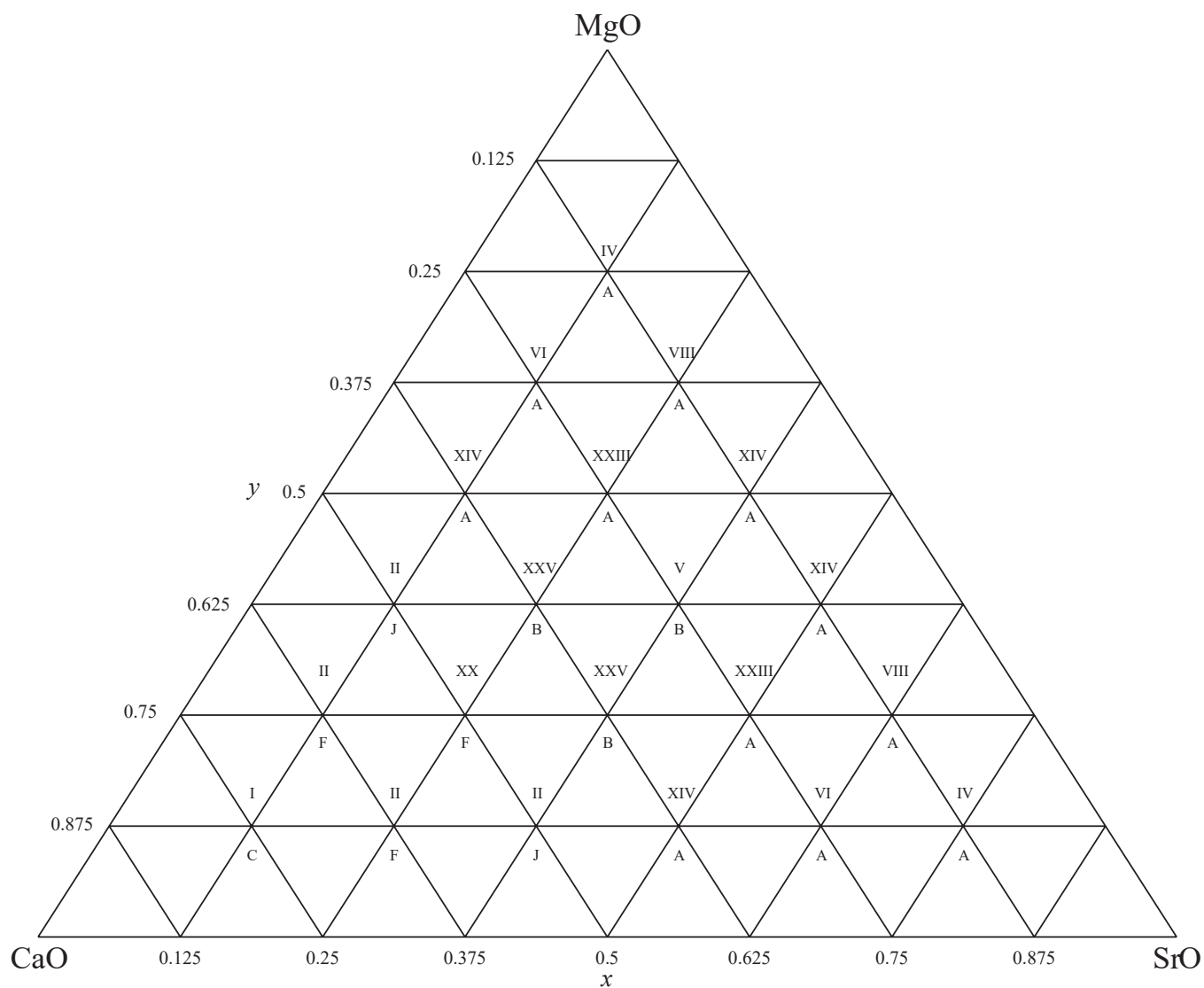
Fig. 7. Phase transition polymorphs in compounds $Mg_{1-y}Ca_{1-x}Sr_{x+y-1}O$ in $B1$- and $B2$-based structures.
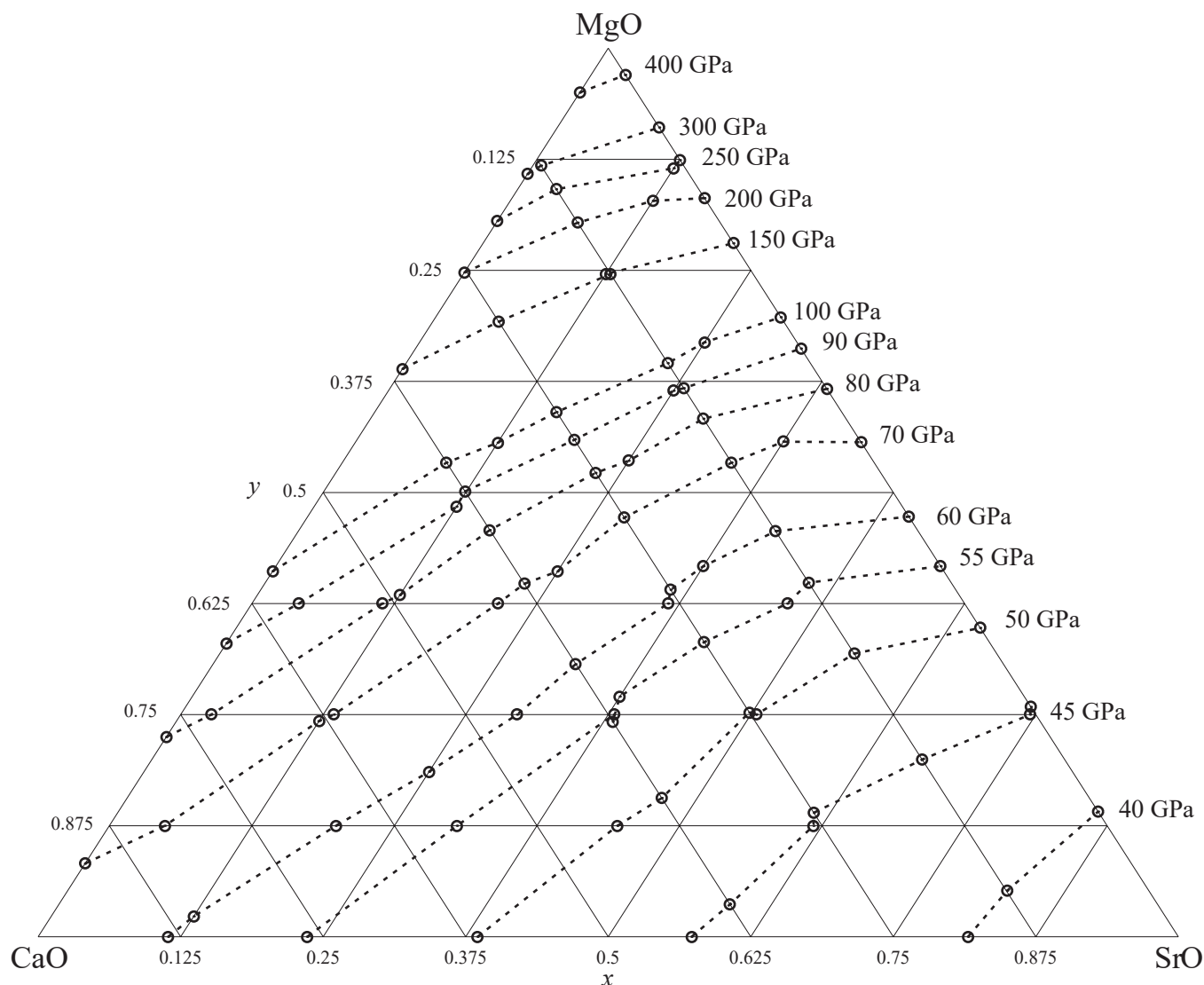
Fig. 8. Phase transitions in compounds $Mg_{1-y}Ca_{1-x}Sr_{x+y-1}O$.

and B2-based structures remains actually in the same ratio when the content of Ca atoms increases, but when the content of Mg atoms increases, it changes to the opposite, i.e., it becomes larger in B1-based structure (Figure 3). Only one of the studied polymorphs, namely $Ca_{0.75}Mg_{0.125}Sr_{0.125}O$, reveals transitions between polymorphs of the same phase, one of which occurs earlier than the transition between polymorphs of different phases, i.e., the B1 – B2 phase transition. This occurs when small amounts of Mg and Sr atoms are added to the CaO compound.

The difference of Ca from Mg and Sr is even more apparent when studying B1 – B2 phase transitions under pressure in compounds dominated by one of the atoms. It turns out that the polymorphs from which the transition occurs (B1-based structure) and the polymorphs into which the transition is made (B2-based structure) in compounds dominated by Ca atoms are completely different from those in compounds dominated by either Mg or Sr atoms. At that, compounds with predominance of Mg atoms are quite similar in this respect to those with predominance of Sr atoms.

CRediT authorship contribution statement

V.V. Pozhyvatenko: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology,

Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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