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Communication

Double perovskites containing hexavalent molybdenum and tungsten: synthesis, structural investigation and proposal of a fitness factor to discriminate the crystal symmetry

Yasutake Teraoka,*[a] Ming-Deng Wei[b] and Shuichi Kagawa[a]

[a] *Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852-8521, Japan. E-mail: yasu@net.nagasaki-u.ac.jp*
[b] *Department of Marine Resources Research and Development, Graduate School of Marine Science and Engineering, Nagasaki University, Nagasaki 852-8521, Japan*

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Double perovskites $A^{II}_2B^{II}B^{VI}O_6$ (A^{II} = Ba, Sr, Ca; B^{II} = Mg, Ni, Co, Cd, Ca; B^{VI} = W, Mo, $W_{0.5}Mo_{0.5}$) have been synthesized and their crystal structures investigated by powder X-ray diffraction measurements. In order to discriminate the crystal systems of the double perovskites, a fitness factor is proposed which corresponds to the size matching between the A cation and the cubo-octahedral cavity formed by eight BO_6 octahedrons. The fitness factor can discriminate the crystal systems of obtained compounds more exactly than the well known tolerance factor.

It is known that hexavalent Mo and W are stabilized not in the primitive ABO_3 perovskites but in the ordered double perovskites, $A^{II}_2B^{II}B^{VI}O_6$,[1,2] in which A^{II} is an alkaline earth ion, B^{II} a divalent metal ion such as Mg, Ca, Co, Ni and Cu, and B^{VI} a hexavalent Mo or W ion. These compounds, in which the charge difference between B^{II} and B^{VI} is four, adopt an ordered structure with the rock-salt arrangement of B^{II} and B^{VI} cations as shown in Fig. 1.[2] Systematic series of $A^{II}_2B^{II}WO_6$ compounds have been so far reported with A^{II} = Ba, Sr and Ca and B^{II} = Mg, Ca, Co, Cu, Fe, Ni and Zn.[1,2] In contrast, reports on Mo-containing double perovskites are limited. The first aim of the present communication is to report the synthesis and structural investigation of Mo-containing double perovskites of $A^{II}_2B^{II}MoO_6$ and $A^{II}_2B^{II}W_{0.5}Mo_{0.5}O_6$ (A^{II} = Ba, Sr, Ca; B^{II} = Mg, Ni, Co, Cd, Ca). The success in the synthesis of the Mo-containing double perovskites and the systematic structural investigation of the Mo and W systems lead to the proposal of a new fitness factor which can discriminate the crystal system of the $A^{II}_2B^{II}B^{VI}O_6$ double perovskites more exactly than the well known tolerance factor.

Polycrystalline powders of double perovskites were synthesized from starting materials of MoO_3, WO_3 and nitrates of other elements. Molybdenum and/or tungsten trioxide was added into a mixed aqueous solution of metal nitrates, and the suspended solution was evaporated to dryness under vigorous stirring. The obtained solid mixture was ground and heat-treated at 623 K for 1 h in order to decompose remaining metal nitrates. After regrinding, the mixture was calcined in air for 5 or 10 h at temperatures varying between 1173 and 1523 K with an interval of 50 K, and the calcination was repeated with regrinding at every interval. Crystal phases in the products were identified by powder X-ray diffraction (XRD) using Cu-Kα radiation (Rigaku RINT-2200VL, 30 kV, 16 mA). Lattice constants were calculated using the PIRUM program.[3] In the syntheses of the double perovskites, $AMoO_4$ and AWO_4 (A = Ba, Sr) were the main and obstinate impurity phases. Calcination for prolonged time or at higher temperatures was repeated until the XRD peak intensities of the impurity phase disappeared or, if present, became as low as possible. The lowest temperature, though with longer calcination period, was adopted as the synthesis condition for each oxide (Table 1).

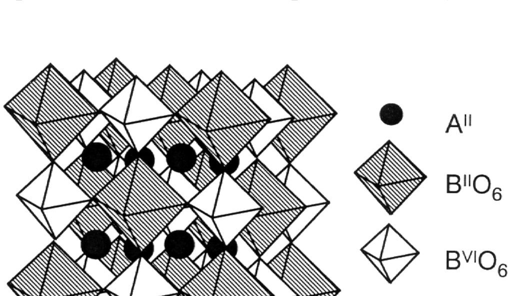

Fig. 1 Crystal structure of $A^{II}_2B^{II}B^{VI}O_6$ double perovskites with the rock-salt ordering of larger B^{II} and smaller B^{VI} cations.

Double perovskites containing Mo were not obtained for A^{II} = Ca but were for A^{II} = Ba and Sr. To the best of our knowledge, the oxides in Table 1, except for $Sr_2B^{II}MoO_6$ (B^{II} = Co and Ni),[4] are new compounds. Compounds with A^{II} = Ba crystallized in the cubic double perovskite structure with the lattice constant close to $2a_p$; a_p is the lattice constant of cubic perovskite of the primitive ABO_3 type ($a_p \approx 4$ Å). XRD patterns of cubic Ba_2CoMoO_6 and $Ba_2CoW_{0.5}Mo_{0.5}O_6$ are depicted in Fig. 2. The appearance of superlattice lines of 111, 311 and 511 evidences the rock-salt ordering of Co^{2+} and Mo^{6+}/W^{6+} ions.[2] The fact that Ba_2CoMoO_6 and $Ba_2CoW_{0.5}Mo_{0.5}O_6$ gave almost the same XRD patterns implies that in the latter oxide W^{6+} and Mo^{6+} ions randomly occupy the smaller octahedra ($B^{VI}O_6$ in Fig. 1) and they form the rock-salt sublattice with larger $B^{II}O_6$ octahedra. As exemplified by the XRD pattern of Sr_2CoMoO_6 (Fig. 2), splitting of some diffraction peaks was observed for all the Sr compounds, and their powder XRD patterns could be satisfactorily indexed with an orthorhombic (B^{II} = Ca) or tetragonal (others) unit cell having a size close to $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$. It was reported[2] that only cubic ($2a_p$) and monoclinic ($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$) unit cells occur in double perovskites with the rock-salt sublattice. Accordingly, it is speculated that the monoclinic distortion of the Sr compounds synthesized in this study, if present, is too small to distinguish the monoclinic system from the orthorhombic and tetragonal systems by powder XRD measurements alone. It is noted here that, in accordance with a previous report,[5] we could discern a monoclinic $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$ unit cell of Ca_2CaWO_6 with a slight distortion ($\beta = 90.18°$).

Fig. 3 shows the relation between the primitive perovskite parameter (a_p) and the ionic radius[6] of divalent B^{II} cations. Values of a_p were calculated from $(V_{UC}/8)^{1/3}$ for cubic oxides

Table 1 Lattice parameters and synthesis conditions of Mo-containing double perovskites

Compound	CS[a]	Lattice parameter/Å	Synthesis conditions
$Ba_2B^{II}MoO_6$			
1 $B^{II}=Ni$	C	$a=8.035(1)$	1373 K, 30 h
2 $B^{II}=Co$	C	$a=8.076(1)$	1273 K, 20 h
3 $B^{II}=Cd$	C	$a=8.3242(9)$	1173 K, 20 h
$Sr_2B^{II}MoO_6$			
4 $B^{II}=Ni$	T	$a=5.5464(7)$, $c=7.892(1)$	1373 K, 40 h
5 $B^{II}=Mg$	T	$a=5.598(2)$, $c=7.875(2)$	1373 K, 60 h
6 $B^{II}=Co$	T	$a=5.562(2)$, $c=7.941(5)$	1423 K, 25 h
7 $B^{II}=Ca$	O	$a=5.753(2)$, $b=5.841(1)$, $c=8.186(3)$	1373 K, 5 h
$Ba_2B^{II}W_{0.5}Mo_{0.5}O_6$			
8 $B^{II}=Ni$	C	$a=8.053(1)$	1273 K, 70 h
9 $B^{II}=Co$	C	$a=8.0928(6)$	1273 K, 60 h
10 $B^{II}=Cd$	C	$a=8.3360(8)$	1173 K, 30 h
$Sr_2B^{II}W_{0.5}Mo_{0.5}O_6$			
11 $B^{II}=Ni$	T	$a=5.587(2)$, $c=7.852(2)$	1423 K, 40 h
12 $B^{II}=Mg$	T	$a=5.603(2)$, $c=7.882(2)$	1373 K, 20 h
13 $B^{II}=Co$	T	$a=5.611(3)$, $c=7.872(4)$	1473 K, 20 h
14 $B^{II}=Ca$	O	$a=5.766(1)$, $b=5.847(1)$, $c=8.183(3)$	1323 K, 60 h

[a]Crystal system: C; cubic, T; tetragonal, O; orthorhombic.

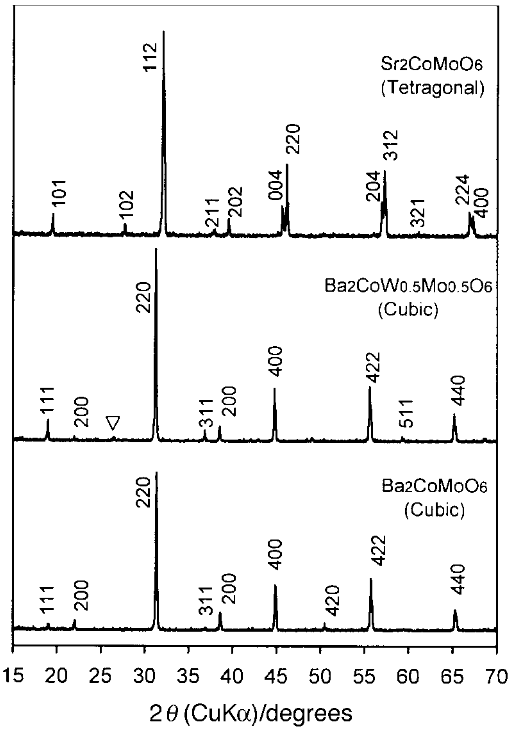

Fig. 2 Powder XRD patterns of $A^{II}_2CoMoO_6$ (A = Ba, Sr) and $Ba_2CoW_{0.5}Mo_{0.5}O_6$. ▽: $BaWO_4$.

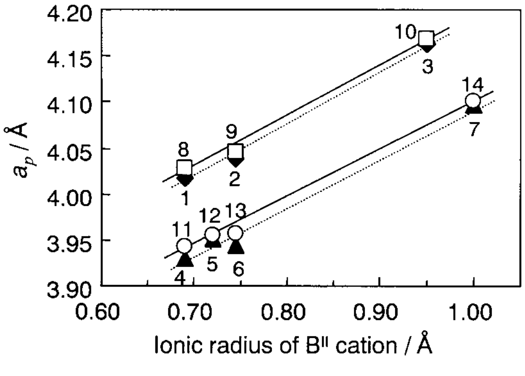

Fig. 3 Primitive perovskite parameter (a_p) of Mo-containing double perovskites as a function of ionic radius of divalent B^{II} cation. See text for the calculation of a_p and Table 1 for the listing of compounds. ◆: $Ba_2B^{II}MoO_6$, □: $Ba_2B^{II}W_{0.5}Mo_{0.5}O_6$, ▲: $Sr_2B^{II}MoO_6$, ○: $Sr_2B^{II}W_{0.5}Mo_{0.5}O_6$.

and $(V_{UC}/4)^{1/3}$ for tetragonal and orthorhombic oxides, where V_{UC} is the unit cell volume of the original double perovskite. As expected, the cell size increases with increasing the radius of B^{II} cations in each series of oxides. The cell size differences of $Ba_2B^{II}B^{VI}O_6 > Sr_2B^{II}B^{VI}O_6$ and $A_2B^{II}W_{0.5}Mo_{0.5}O_6 > A_2B^{II}MoO_6$ are also consistent with ionic size differences[6] of Ba > Sr and W > Mo.

In parallel with the investigation of the Mo-containing double perovskites, the synthesis and structural investigation of the W analogues have been carried out. The following compounds were obtained, and their crystal systems were in accordance with the literature.

($2a_p$)-type cubic phase; $Ba_2B^{II}WO_6$ (B^{II} = Ni,[7] Co,[7] Cd,[8] Ca[7])

($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$)-type tetragonal phase; $Sr_2B^{II}WO_6$ (B^{II} = Ni,[7] Mg,[8] Co,[7] Cd)

($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$)-type orthorhombic phase; Sr_2CaWO_6,[9] $Ca_2B^{II}WO_6$ (B^{II} = Ni, Co)[1]

($\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$)-type monoclinic phase; Ca_2CaWO_6[5]

The Goldschmidt tolerance factor (t)[10] is often used to predict the formation of perovskites and the crystal symmetry for a given pair of A- and B-site cations. The tolerance factor is given by

$$t=(r_A+r_O)/\sqrt{2}(r_B+r_O) \qquad (1)$$

where r_X is the ionic radius[6] of X ion, and $r_B=(r_{B^{II}}+r_{B^{VI}})/2$ for $A_2B^{II}B^{VI}O_6$ double perovskites. The relation between the t value and the crystal symmetry is depicted in Fig. 4A. All of the Ba compounds with t values >0.96 are cubic. In each series of the Sr and Ca compounds, oxides with the smallest t values (B^{II} = Ca) have unit cells with lower symmetry than the others; orthorhombic *vs.* tetragonal for the Sr compounds, and monoclinic *vs.* orthorhombic for the Ca compounds. In this way, the t value can discriminate the crystal symmetry in the series of each A^{II} cation. When all the compounds are taken into account, however, overlap regions exist. At t values between 0.95 and 1.0, both the cubic (Ba compounds) and tetragonal (Sr compounds) systems occur, and the t value of tetragonal Sr_2CdWO_6 is smaller than those of orthorhombic $Ca_2B^{II}WO_6$ (B^{II} = Ni, Co). This suggests that a new parameter, which reflects more pronouncedly the size difference of A site cations, is necessary to exactly discriminate the crystal system of double perovskites. For this purpose, we propose a new fitness factor (Φ) defined by eqn. (2).

$$\Phi=\sqrt{2}r_A/(r_B+r_O) \qquad (2)$$

For the ideal cubic unit cell of the primitive ABO_3 type (t = 1.0, $r_A=r_O$), the B–O interionic distance, r_B+r_O, is equivalent

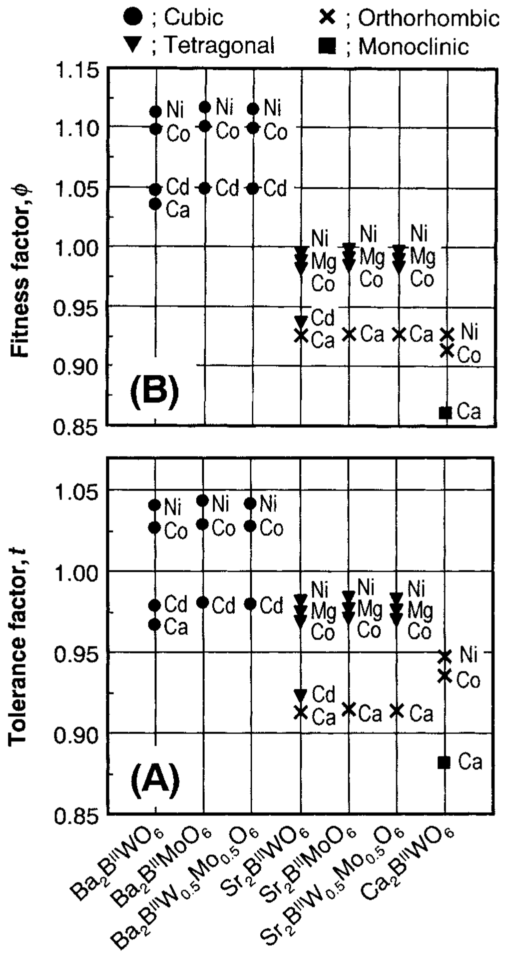

Fig. 4 Tolerance factor (A) and fitness factor (B) for discriminating unit cell systems of $A^{II}_2B^{II}B^{VI}O_6$ double perovskites.

to half of the cell edge and $r_A/(r_B+r_O)$ is equal to $1/\sqrt{2}$ ($\Phi=1.0$). This parameter corresponds to size matching between the A cation and the cubo-octahedral cavity formed by eight BO_6 octahedrons. As shown in Fig. 4B, the Φ factor can exactly discriminate the crystal system. By introducing the fitness factor, the borderline between the cubic Ba compounds and the tetragonal Sr compounds becomes clear. In addition, all of the orthorhombic Sr and Ca compounds have similar Φ values, giving a clear borderline at $\Phi=0.93$ to distinguish from tetragonal systems. The cubic system occurs at $1.00<\Phi$, the tetragonal system at $0.93<\Phi<1.00$, the orthorhombic system at $0.90<\Phi<0.93$, and the monoclinic system at $\Phi<0.90$; the borderline value of $\Phi=0.90$ between orthorhombic and monoclinic systems is not definitive owing to lack of data.

The reduction of crystal symmetry of perovskites usually results from the tilting of BO_6 octahedrons.[2,11] When an A cation is closely packed in the cubo-octahedral cavity ($\Phi \geqslant 1$), tilting would be suppressed and the cubic system results. At $\Phi<1$ with the loose packing of the A cation, tilting of BO_6 octahedrons or distortion would be expected, and would become larger with decreasing Φ. It is well known that B site vacancies in perovskite-type oxides are rare, while those at A sites are commonly found in, for example, ReO_3, Na_xWO_3[12] and $La_{2/3}TiO_3$.[13] This indicates that the framework made of BO_6 octahedra is of primary importance for the construction of the perovskite structure and that A site cations stabilize the structure by sitting in the cubo-octahedral cavities. The concept of the proposed fitness factor is in line with this.

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