Ternary Transition Metal Oxide Phases of the Fluorite Structure

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The cubic fluorite structure (C 1 type) occurs frequently among the following four kinds of compounds.

1) Halides, especially fluorides, of the larger divalent cations and combinations of univalent and tri-, quadri- or hexavalent cations.

2) Oxides, sulfides, selenides and tellurides of univalent ions, mostly alkalis. If the general formula is written AX_2 , the atom A is here the negative rather than the positive ion — the antiferite arrangement.

3) Oxides of large quadrivalent ions.

4) Intermetallic compounds.

The A and X atoms occupy the following positions in the space-group $O_h^{5-}Fm3m$:

4 A atoms in 4(a) $0,0,0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}$
 8 X atoms in 8(c) $\pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{1}{4}, \frac{1}{4}; \frac{3}{4}, \frac{3}{4}, \frac{3}{4})$

Each A atom is situated at the centre of a cube of eight X atoms located at the corners, and each X atom is tetrahedrally surrounded by four A atoms. The crystal is of an unsymmetrical valence type. From a geometrical point of view A—X contact is obtained when the radius ratio $r_A/r_X \geq \sqrt{3}-1 = 0.73$. This relation is also fulfilled or nearly so for all compounds of the C 1 type, earlier reported, with the exception of the high temperature modification of ZrO_2 ¹ for which the ratio r_A/r_X is 0.66, if Goldschmidt's radii values are chosen.

The only quadrivalent ions, for which the geometrical condition for the formation of a stable dioxide lattice of the C 1 type is fulfilled, are found among the rare earth metals and the actinides. The existence of oxide phases of the fluorite structure has been well established in the following cases:

CeO_2 ^{2,3}, PrO_2 ^{4,5}, ThO_2 ⁶, PaO_2 ⁷, UO_2 ^{2,8,9}, NpO_2 ¹⁰, PuO_2 ¹¹, and AmO_2 ^{7,12}.

The isomorphous high temperature modification of ZrO_2 has been reported to be stabilized at room temperature at the presence of fairly small amounts of MgO in the lattice. The saturated mixed crystal of ZrO_2 with MgO was proposed to correspond to the formula $Mg_2Zr_3O_8$ ^{13,14} or $MgZr_3O^{14}$. According to Ruff and Ebert¹⁴ the atoms occupy the following positions in the cubic unit cell

with the lattice constant $a = 5.08 \text{ \AA}$: 2 Mg in $0,0,0$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, 3 Zr in $0, \frac{1}{2}, \frac{1}{2}$; $\bar{1}, \bar{1}, \bar{1}$, and 8 O in $\pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \bar{1}, \bar{1}, \bar{1})$. This structure is most unlikely, however, partly because of some extremely small interatomic Mg-Zr distances and partly because such a configuration is not in any way consistent with a diffraction pattern of a face-centered lattice.

In the present investigation ternary oxide phases of the C 1 type (defective lattice) containing two transition metals A and B — where B = Ti or Zr — were prepared in two ways.

1) Binary A, B alloys of different compositions, sintered in zirconia crucibles in a high-frequency vacuum induction furnace, were finely powdered and oxidized with steam in the presence of hydrogen in great excess at temperatures between 600°C and 800°C .

2) Oxides of the two transition metals were mixed in different proportions and heated in evacuated and sealed silica tubes at temperatures between 700°C and 1100°C .

Since the double-oxides of the C 1 type could not be prepared in a pure state, the composition of the phases could not be determined with any accuracy. The purest samples were obtained from method 1 (binary oxides as impurities), while only very small amounts of these oxides could be prepared according to method 2. Attempts to synthesize them from binary oxides in a vacuum furnace at temperatures between 1200°C and 1800°C were in vain, probably due to the instability at these high temperatures.

The phase analysis of the samples was performed by means of powder photographs taken with Cu- $K\alpha$ radiation in cameras of the Guinier type.

Black ternary oxides of the fluorite structure were found to exist with the following combinations of atoms: A = Fe, Co, Ni and B = Ti, A = V, Cr, Mo, W, Mn and B = Zr. No similar oxides were obtained in the cases of A = V, Cr, Mn, Fe, Co, Ni and B = Nb, Ta, Mo, W. The lengths of the cubic axes were measured to have the same approximate values for all the phases and to vary between $a = 5.09 \text{ \AA}$ and $a = 5.13 \text{ \AA}$, which together with the phase analysis from the powder photographs indicates comparatively large homogeneity ranges. The intensities of the diffraction lines were observed to agree well with the $p|F|^2$ values calculated for a disordered distribution of the A and B atoms over the four-fold atomic position. As pointed out above the phase composition could not be determined with any certainty, but the A/B ratio seems to lie within the approximate limits $1/3 \lesssim A/B < 1$ for all the oxides reported. As the Ti and Zr atoms in all probability are ionized to the quadrivalent state the general formula can be written as $A_K^{z+} B_{4-K}^{4+} O_{8-K/2(4-z)}$, where z^+ designates the valency of the A component and has a maximum value of 4 if all metal atom positions are assumed to be occupied. As $1 \lesssim K < 2$ in the formula, some oxygen positions will be empty for $z < 4$. If $z > 4$, which may be the case for A = V, Mo and W, all oxygen positions would in all probability be occupied and some metal atom sites be empty.

For $z = 2$ and $K = 2$ in the general formula given above, the phase composition ABO_3 is obtained, meaning compounds of the ilmenite structure (E 2_2 type)¹⁵, when A = Mn, Fe, Co, Ni and B = Ti. No analogous compounds were found to exist for A = V—Ni and B = Zr, Nb, Ta, Mo, W, although

phases related to the corundum structure (D 51 type)¹⁶ were obtained in the cases of A = Cr and B = Mo and W¹⁸. The perovskite structure (E 2₁ type)¹⁷ also has the composition ABO₃ but with one divalent and one quadrivalent metal ion rather than two trivalent ions as in the ilmenite structure. No phase of the E 2₁ type could be found in the A—B—O systems which were investigated. The oxide phases of the C 1 type reported above all seem to have the A/B ratio smaller than unity and the oxygen content greater than that corresponding to 3/2 oxygen atoms per metal atom. The latter relation is accentuated by the fairly large volume per metal atom (about 33.5 Å³) as compared, for instance, with that of ilmenite (26.2 Å³).

The reported ternary oxide phases of the C 1 type all have a mean lattice constant of $a = 5.11$ Å giving interatomic O—A,B (4-coordination) and O—O (6-coordination) distances of 2.21 and 2.56 respectively. As the radius ratio $r_{\text{Ti}^{4+}}/r_{\text{O}^{2-}} = 0.48$ is considerably smaller than that calculated for anion-cation contact in the C 1 lattice, 0.73, the Ti—O distances are greater than those observed for rutile¹⁹, anatase²⁰ and brookite²¹, about 1.95 Å. The Zr—O distances in baddeleyite²² — of a slightly deformed C 1 type — vary between 1.95 and 2.65 Å. The smallest O—O distances observed for all metal oxides seem to be near 2.55 Å, and this gives an explanation to the fact that the dioxides of the fluorite structure where the radius ratio between the cations and the anions is smaller than 0.73 have approximately the same lattice constant, about 5.11 Å (corresponding to O—O distances of 2.56 Å).

SUMMARY

Ternary A—B—O phases of the C 1 type, where A and B are transition metals, have been prepared by different methods and investigated by X-ray methods. The general formula of these compounds is proposed to be $A_K^{z+}B_{4-K}^{4+}\text{O}_{8-K/2(4-z)}$, where A = Fe, Co, Ni in combination with B = Ti and A = V, Cr, Mo, W, Mn in combination with B = Zr; K varies to some extent within the approximate limits $1 \lesssim K < 2$, and z^+ designates the valency of the A component. All the oxides are black and have the same axial lengths, varying between $a = 5.09$ Å and $a = 5.13$ Å, which corresponds to mean interatomic A,B—O and O—O distances of 2.21 Å and 2.56 Å respectively. The oxides are stable at room temperature in spite of unfavourable geometrical conditions for the formation of a lattice of the C 1 type.

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