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Defect pyrochlore structure $A_2B_2X_6$: a general approach to the coordination polyhedra around the metal ions

A. JEREZ, M. L. LÓPEZ, S. GARCÍA-MARTÍN, M. L. VEIGA, C. PICO
Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

On the basis of the distances A–X and B–X, in the defect pyrochlores $A_2B_2O_6$, a general approach to the coordination polyhedra around A and B metal ions is established. Results show that, depending on these distances, coordination of 3 + 3 and 3 + 3 + 3 around A ions can be found and that a region of low stability should exist.

1. Introduction

The pyrochlore structure is adopted by minerals with the general formula NaCa(Nb, Ta)$_2$O$_6$(OH, F) and a large number of other compounds (essentially, fluorides, oxyfluorides and oxides). The structure is cubic (space group Fd3m, no. 227, $Z = 8$) and can be regarded as an anion-deficient fluorite [1] which retains the face-centred cubic lattice. This description is achieved by removing 1/8 of the anions in an ordered fashion, such that one-half of the cubic polyhedra contain vacancies at two opposing corners. Alternative descriptions of the structure are reviewed elsewhere [2].

With a general composition $A_2B_2X_6Y$ the A ions retain the eight-fold coordination but the B ions are only in six-fold coordination. Thus, the A ions are larger than the B ions in compounds with this structure. The coordination polyhedra of the ions in the ideal case are AX_6Y_2, BX_6, XA_2B_2 and YA_4. By removing combination of A and Y ions [3], a variety

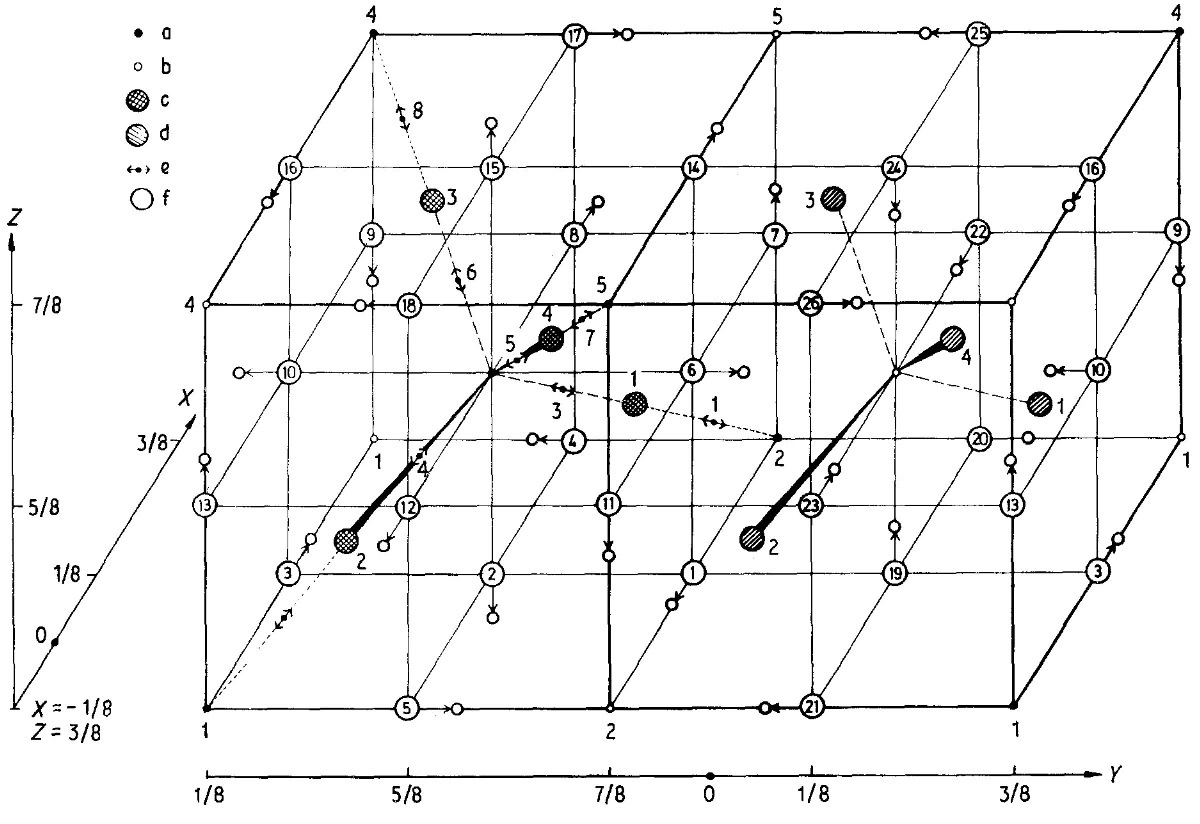

Figure 1 Spacial arrangement of the *a*, *b*,*c*, *d*, *e* and *f* positions in the pyrochlore structure.

of deficient structures can be produced which are known to occur with the general formula $A_{1-2}B_2X_6Y_{0-1}$.

Chakoumakos [3] has examined the geometry of the ideal pyrochlore structure and the purpose of the present work was to establish a general approach to the defect pyrochlore structures. Using the structural basis discussed here, the stereochemistry of the metal ions in this structure type can be defined without ambiguity.

2. Geometry of the pyrochlore structure type

All the atoms in the pyrochlore unit cell occupy special positions in the space group Fd3m (no. 227, origin at 16*c*, 3m). For the $A_2B_2X_6Y$ stoichiometry, these positions are 16*d* (for B), 48*f* (for X) and 8*a* (for Y). Thus, A ions are practically confined to the 16*c* positions. The atomic arrangement is completely specified except for the *u* coordinate of the 48*f* positions. Fig. 1 shows the spatial arrangement of *a*, *b*, *c*, *d* and *f* positions; the arrows indicate the displacements of the *f* positions when *u* varies from $u = 0.375$ (ideal arrangements as in the anion deficient fluorite) to $u = 0.4375$. Therefore, the B site (16*d*) becomes a regular octahedron (defined by the X anions numbered as 10, 13, 23, 16, 24, 26 around 4, for example, in the right hand of Fig. 1) and cubic A site (16*c*) distorts into a trigonal scalenohedron (X labelled as 6, 11, 12, 14, 15, 18 around 4, for example left of Fig. 1).

Nevertheless, in deficient pyrochlores $A_{1-2}B_2O_6$, new possibilities of situation for the A ions arise from the fact that B ions occupy the 16*d* positions and 8*a*,

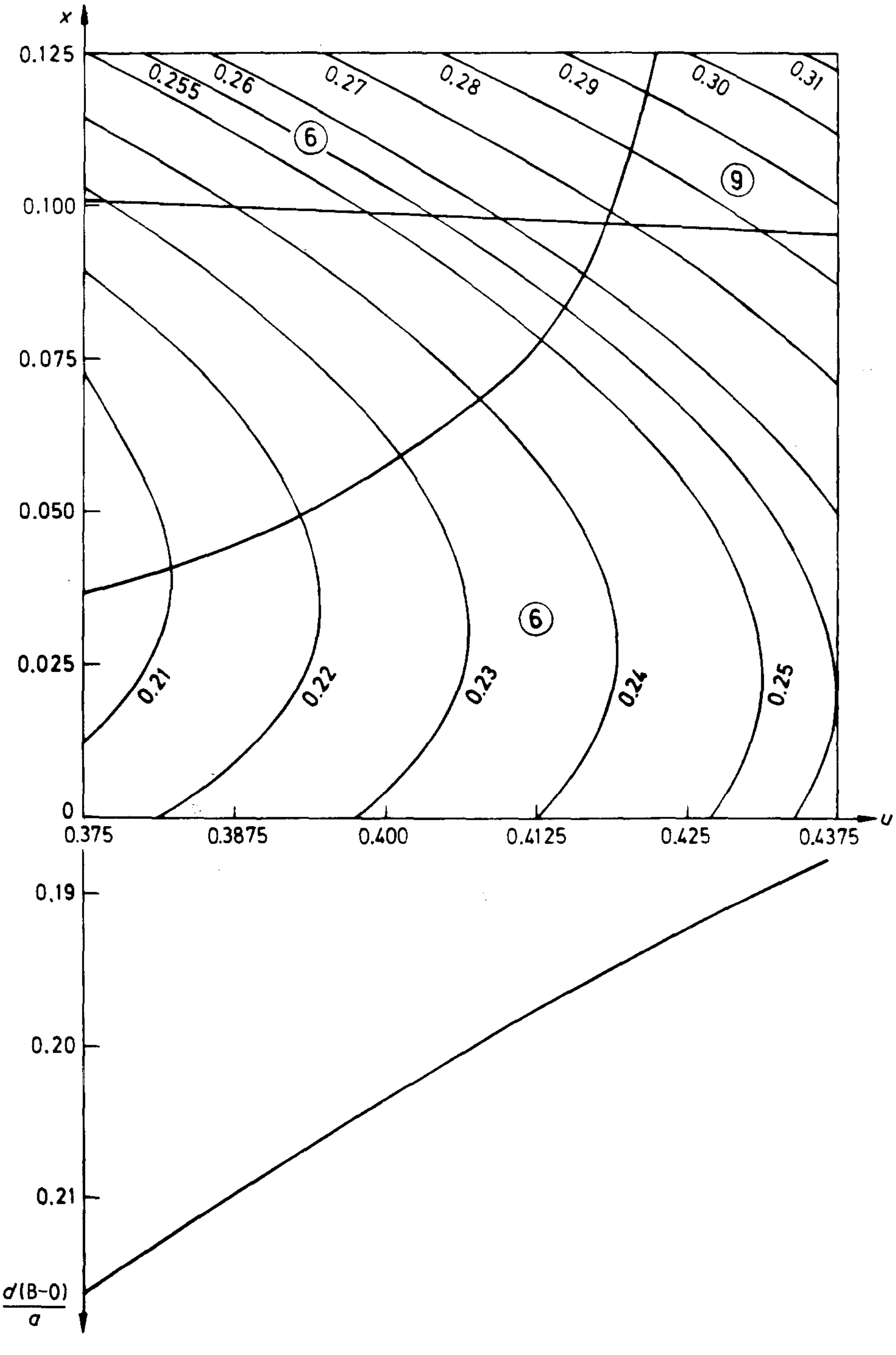

Figure 2 Dependence of *u* (lower curve) and *x* (upper curves) on the anion–cation distances.

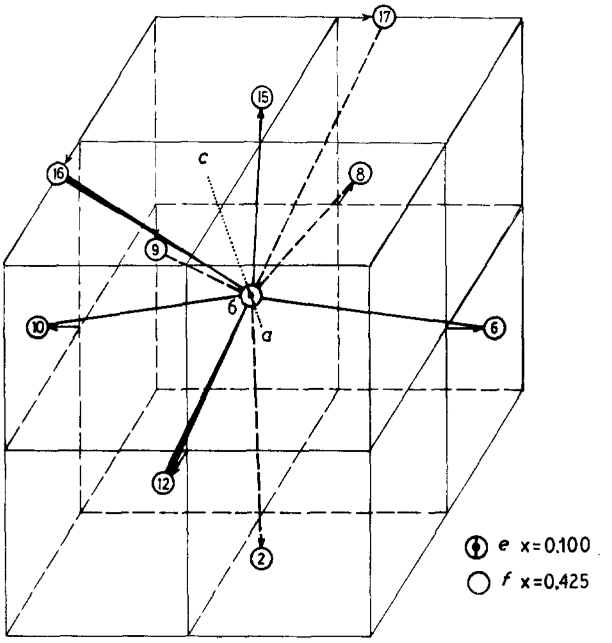

Figure 3 Nearest 3 + 3 + 3 *f* positions around a given *e* position.

16*c* and 32*e* ones are aligned (as is showed in Fig. 1, in which *e* positions are represented with double arrows). Then it is necessary to introduce a new parameter, the x coordinate associated with the *e* positions, so that for $x = 0$, *e* positions are the same as *c* ones (leading to the arrangement found in the ideal pyrochlores) and for $x = 0.125$, *e* positions are superimposed with the *a* ones (occupied by the A ions in the "inverse" pyrochlores). Thus it is possible to analyse the position of A in the structure as a function of the value of this parameter.

As the effective size of the A sites will depend on both u and x values, and the size of B sites (16*d*) is only a function of u, we can suppose that u is essentially determined by the B–X distance (which in a first approach is considered equal to the sum of the ionic radii). A ions are accommodated along the *a*–*e*–*c* axis depending on the size of the site. When u is approximately fixed, the location of A ions is determined by the x parameter.

In this way, we can predict u and x values for a given defect pyrochlore on the basis of the A–X and B–X distances, obtained from the respective sums of the ionic radii. Fig. 2 shows the dependence of both structural parameters with respect to the bond distances. The lower curve is constructed according to the relation (a is the cell parameter)

$$\frac{d(\mathrm{B{-}X})}{a} = (u^2 - u + 9/32)^{1/2} \qquad (1)$$

and the upper curves according to the distance from *e* to the three nearest *f* positions, given by the relation

$$\frac{d(\mathrm{A{-}X})}{a} = [(u + x - 1/4)^2 + 2(1/8 - x)^2]^{1/2} \qquad (2)$$

(values of $d(\mathrm{A} - \mathrm{X})/a$ are above each curve).

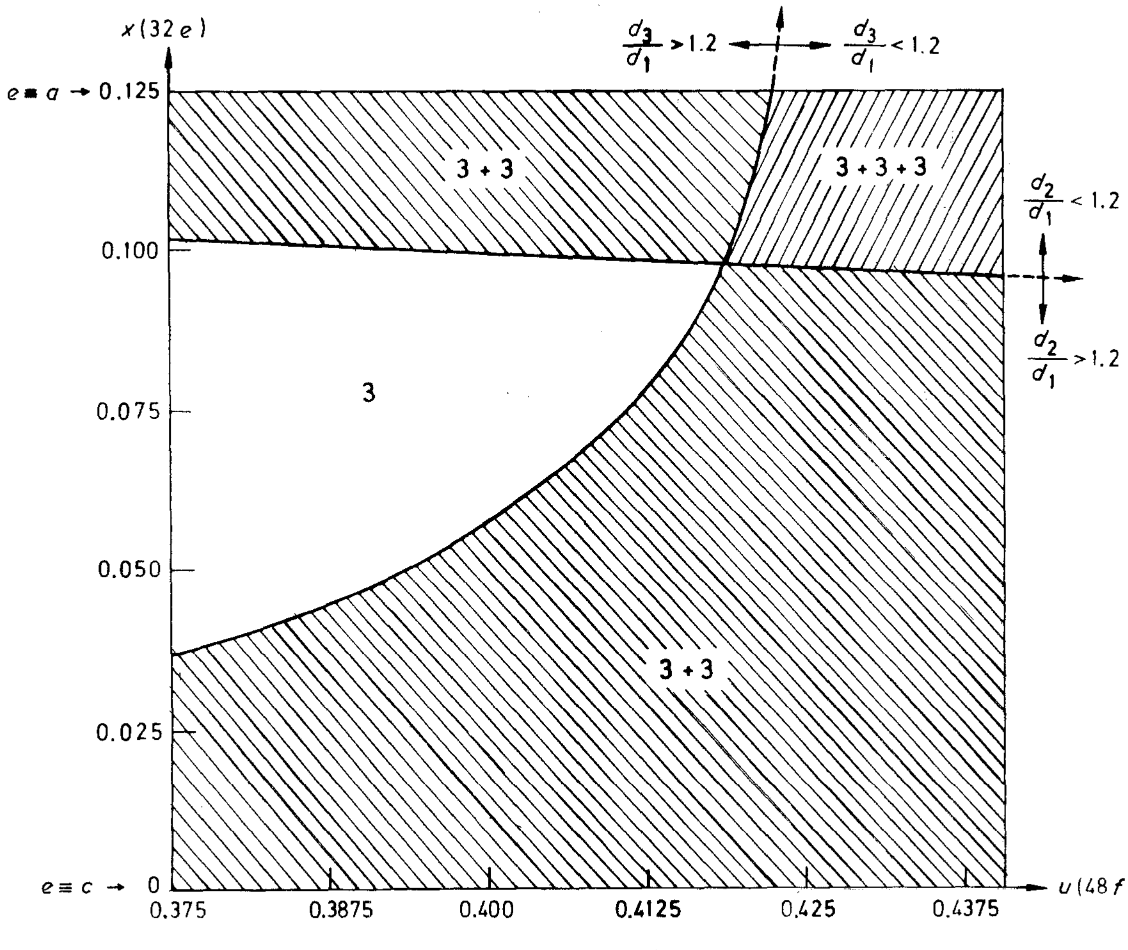

Figure 4 The variation of coordination number around *e*, with *u* and *x* positional parameters.

TABLE I Parameters, *u* and *x*, and A–O distances in pyrochlores $A_2B_2O_6$

Compound	*a* (nm)	*u* (nm)	x (nm)	*d* (A–O) (nm)			*d* (B–O) (nm)	Reference
$TlNbTeO_6$	1.0262	0.0434	0.0092	0.354(2)	0.287(3)	0.328(8)	0.1936	[4]
$KNbTeO_6$	1.0249	0.0427	0.0086	0.354(2)	0.375(4)	0.219(7)	0.1960	[5]
$RbNbTeO_6$	1.0257	0.0428	0.0102	0.354(4)	0.284(6)	0.238(9)	0.1958	[5]
$CsNbTeO_6$	1.0294	0.0430	0.0115	0.325(7)	0.304(0)	0.355(7)	0.1957	[5]
$KMoSbO_6$	1.0277	0.0424	0.0090	0.346(2)	0.275(5)	0.223(1)	0.1968	[6]
$RbMoSbO_6$	1.0255	0.0425	0.0104	0.330(6)	0.287(7)	0.340(0)	0.1969	[6]
$CsMoSbO_6$	1.0300	0.0432	0.0109	0.334(5)	0.301(7)	0.348(2)	0.1947	[6]
$TlMoSbO_6$	1.0240	0.0427	0.0100	0.336(8)	0.285(9)	0.335(2)	0.1958	[6]
K_2GeTeO_6	0.9417	0.0424	0.0101	0.322(3)	0.275(4)	0.325(1)	0.1910	[7]
Rb_2GeTeO_6	0.9946	0.0426	0.0113	0.312(2)	0.288(5)	0.341(0)	0.1911	[7]
Cs_2GeTeO_6	1.0012	0.0433	0.0120	0.313(1)	0.303(4)	0.353(6)	0.1890	[7]

Thus, from the reduced B–X distance found from the ordinate axis, we can find the *u* value on the abscissa. The upper curve corresponding to the reduced A–X distance will show the probable *x* value.

In Fig. 3 the nine (3 + 3 + 3) nearest *f* positions around the aligned *a–e–c* sites are shown (reference numerals are the same as in Fig. 1). The shortest distances correspond to the 8, 10 and 15*f* positions, and are given by Equation 2.

The distances to the next-nearest neighbours are obtained from Equations 3 and 4

$$f_{9,16,17}\frac{d(\text{A–X})}{a} = [(u - x - 1/4)^2 + 2(1/8 + x)^2]^{1/2} \tag{3}$$

$$f_{2,6,12}\frac{d(\text{A–X})}{a} = [(u - x)^2 + 2(1/8 - x)^2]^{1/2} \tag{4}$$

Depending on the position of the A ion along the *a–e–c* axis (i.e. the value of the *x* positional parameter), these ions will be surrounded by 3, 6 (3 + 3) or 9 (3 + 3 + 3) anions lying in the referred *f* positions. If we take the shortest distance (Equation 2) as equal to the sum of the ionic radii, we can establish the coordination polyhedron around A on the basis of the relation between the other distances and this sum. For instance, if we consider, as bond lengths, distances with an increase of not more than 20% over the shortest one, we can obtain the representation shown in Fig. 4, in which three zones can be seen, corresponding to 3, 3 + 3 and 3 + 3 + 3 coordinations around the A ions.

Table I gives some examples of pyrochlores AB_2O_6 which fit the proposed model. Evidently, a 3-coordination around A ions should determine a low stability of the structure. In this region one can expect that pyrochlore compounds should not exist or, at least, the A–X and B–X distances should be larger than the sum of the ionic radii leading to *x* and *u* positions that permit 3 + 3 coordination around A.

From this analysis is it possible to establish unambiguously the stereochemistry of A and B ions in a pyrochlore-type structure as a function of *x* and *u* geometrical parameters.

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