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Prediction of Anion Distributions Using Pauling's Second Rule

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Pauling's second crystal rule is shown to be able to predict in a general and simple way the distribution of anions in mixed oxyanion systems such as oxynitrides and oxyhalides with diverse compositions and structure types. Results are presented in a plot correlating the charge of the anions obtained from the observed occupancies in crystallographic positions with the calculated bond strength sums for these sites.

In recent years, different mixed oxyanion systems have been investigated with the aim of finding novel materials showing interesting physical properties or completely new crystal structures. Substitution of oxygen by nitride in silicates leads to the nitridosilicates showing exceptional thermal and chemical stability, high hardness, and mechanical strength.[1,2] Ga_3O_3N with spinel structure is an example of oxynitride that has been recently reported as a new photoluminiscent material.[3] Transition metal oxynitrides such as $TiO_{2-x}N_x$[4] and TaON[5] have shown improved photocalytical activity with respect to titanium and tantalum oxides. Substitution of oxide by nitride in perovskites allows the stabilization of this structural type in some oxide systems, also leading to new interesting materials.[6] For instance, perovskite tantalum oxynitrides with the formula $Ca_{1-x}La_xTaO_{2-x}N_{1+x}$ have been reported as nontoxic red-yellow inorganic pigments,[7] and $BaTaO_2N$ and $SrTaO_2N$ show high bulk dielectric constants.[8] Oxynitrides have also been reported as new anode materials for rechargeable lithium batteries, showing high reversibility and capacity, as well as enhanced chemical stability with respect to nitrides.[9] In the field of superconductors, complex copper oxyhalides with perovskite-related structures have been widely investigated[10] and manganese oxychlorides have been reported as suitable magnetoresistive materials.[11]

Anion ordering in mixed anion systems has been discussed extensively,[12−14] not only from an academic point of view but also because of its potential relevancy in determining the physical properties. Electronic and anionic conductivity may be affected by the anion distribution. For instance, the capacity for discharge, as well as the reversibility in lithium chromium oxynitrides, is severely affected by the disorder of anions.[15] Disorder of anions may also induce electron localization in layered oxynitrides as $Sr_2NbO_{4-y}N_y$.[16,17]

The distribution of anions in oxynitrides and oxyfluorides is difficult to determine using X-ray diffraction data because of the small differences in the scattering lengths of N, F, and O. Use of neutron diffraction data allows this problem to be solved in the case of oxynitrides but not in oxyfluorides because of the similar neutron scattering lengths of F and O.

Quantitative a posteriori approaches to determine or to understand the distribution of anions in mixed oxyanion systems have been based in the bond valence method,[18,19] calculations of the total energy,[12] and calculations of the Madelung part of lattice energy.[20,21] All these methods need a previous knowledge of the crystal coordinates. Bond valence sums[18] are used systematically as a powerful tool to check on the reliability of a determined structure and have

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Table 1. Bond Strength Sums and Ordering Schemes for Anion Sites in Representative Examples of Oxynitrides and Oxyhalides[a]

compound	structure type	ordering scheme or coordination preferences	average charge of anions, $\bar{\zeta}$	bond strength sums (b) for anion sites
Sr_2TaO_3N	K_2NiF_4	O_{axial}, $[N,O]_{equatorial}$	2.25	axial, 1.94; equat, 2.55
$Sr_2NbO_{3.28}N_{0.72}$	K_2NiF_4	O_{axial}, $[N,O]_{equatorial}$	2.18	axial, 1.90; equat, 2.46
$Ca_2CuO_2Cl_2$	K_2NiF_4	Cl_{axial}, $O_{equatorial}$	1.50	axial, 1.10; equat, 1.56
K_2NbO_3F	K_2NiF_4	$[F,O]_{axial}$, $O_{equatorial}$	1.75	axial, 1.38; equat, 2.11
Nd_2AlO_3N	K_2NiF_4-related	$[N,O]_{axial}$, $O_{equatorial}$	2.25	axial, 2.17; equat, 2.33
Sr_2MnO_3Cl	K_2NiF_4-related	$[Cl,O]_{axial}$, $O_{equatorial}$	1.75	axial, 1.61; equat, 1.88
$Sr_2CuO_2F_2$	K_2NiF_4-related	F_{axial}, $O_{equatorial}$	1.50	axial, 1.44; equat, 1.56
$Sr_2NdCu_2O_5F$	Ruddlesden−Popper $n = 2$	$[F,O]_{axial}$, $O_{equatorial}$	1.83	axial, 1.50; equat, 1.99
$Sr_3Co_2O_5Cl_2$	Ruddlesden−Popper $n = 2$	$[Cl,O]_{axial}$, $O_{equatorial}$	1.71	axial, 1.61; equat, 1.88
$Sr_4Mn_3O_8Cl_2$	Ruddlesden−Popper $n = 3$	Sr−Cl,O; Mn−O,Cl	1.80	O, 1.98,1.77,1.67; Cl, 1.71
$Li_{14}Cr_2N_8O$, $Li_{16}Nb_2N_8O$	antifluorite	Li−O; Cr−N; Nb−N	2.89	N, 3; O, 2
TaON, NbON	baddeleyite	Ta(Nb)−O,Ta(Nb)−N	2.50	N, 2.86; O, 2.14
$Li_6Ca_{12}Re_4N_{16}O_3$	modified Th_3P_4	Li−N,O; Ca−N,O; Re−N	2.84	N, 3.10, 3.03; O, 1.73
Ge_2N_2O, Si_2N_2O	tetrahedral framework	Si(Ge)−N,O	2.67	N, 3; O, 2
KGeON	Wurtzite-related	Ge−N,O; K−O,N	2.50	N, 3.2; O, 1.8
LiSiON	Wurtzite-related	Si−N,O; Li−O,N	2.50	N, 3.25; O, 1.75
$Sr_6Li_2Cr_2N_8O$	polyhedral framework	Sr,Li−O;Cr−N	2.89	N, 3.12, 3.07, 2.99, 2.95; O, 1.73
Sr_4MoN_4O	layered	Sr−O, Mo−N	2.80	N, 3.07, 2.83; 3.12, 2.74, 2.45, 2.5; O, 1.95, 2.0
$Tl_2Zr_3OF_{12}$	layered	Tl−F; Zr−O,F	1.08	O, 1.5; F, 0.83, 1.17, 1.0
Sr_3GaO_4F	layered	Sr−O,F; Ga−O	1.80	O, 1.9; F, 1.4
$Sr_2Cu_3O_4Br_2$	layered	Cu−O,Br; Sr−Br,O	1.67	O, Br, 1.67
Ba_3ZnN_2O	framework, linear ZnN_2	Ba−N,O; Zn−N	2.67	N, 2.93; O, 2.13
Sr_4GaN_3O	slabs, triangular GaN_3	Sr−O,N; Ga−N	2.75	N, 3, 2.67; O, 2.33

[a] See the Supporting Information for a full table with the list of parameters represented in Figure 1 and the reference corresponding to each compound.

been frequently applied to oxyfluorides.[19] For oxynitrides, energy calculations, as well as qualitative approaches based on the differences in electronegativities and polarizabilities of O and N, have been used.[22] In some particular examples, the satisfying of Pauling's second crystal rule[23] has been applied to understand the reasons of the observed anion ordering scheme.[16,24,25]

In this paper, we show that Pauling's second crystal rule is able to predict in a general and simple way the distribution of anions with different charge in systems as oxynitrides with diverse structure types and compositions, as well as in oxyhalides. Results are shown using a plot correlating the charge of the anion in a given site, obtained from the observed occupancies in the crystal structure, with the calculated bond strength sum for this site.

Pauling's second crystal rule (PSCR) states:[23] "In a stable coordination structure the electric charge of each anion tends to compensate the strength of the electrostatic valence bonds reaching to it from the cations at the centres of the polyhedra of which it forms a corner", that is, for each anion, the charge q tends to be equal to the bond strength sum (b):

$$b = \sum_i \frac{z_i}{\nu_i}$$

where z_i is the formal oxidation state of each cation bonded to a given anionic position and ν_i is its coordination number.

We have calculated the bond strength sums (b) for each anionic position in representative examples of oxynitrides and in oxyhalides. Table 1 lists these compounds together with their anion ordering scheme, the bond strength sums, the charge (q) in each anion position determined from the experimental anion distributions, and the average charge for anions ($\bar{\zeta}$). In Figure 1, we have represented the difference between the charge, q, of the anion occupying a given position (i.e., $q = -3$ for N, -2 for O, and -1 for halide) and the average charge of anions. For mixed sites occupied by two anions with different charge, q is the average charge according with the observed occupancy factors. On the x axis we have represented the difference between the bond strength sums and the average charge of anions. The line in Figure 1 shows the ideal correlation $b - \bar{\zeta} = q - \bar{\zeta}$ that represents the satisfying of PSCR, where the average charge

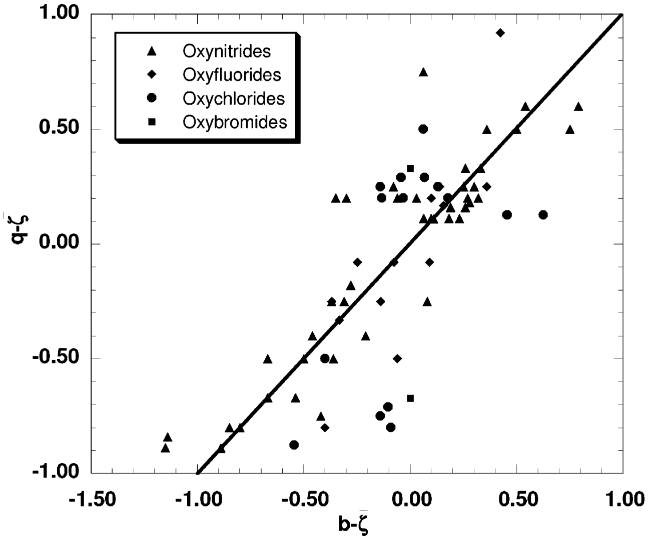

Figure 1. Plot of the experimentally determined charge of the anion versus the bond strength sum in each site, both corrected for the average charge of anions, $\bar{\zeta}$, for oxynitrides and oxyhalides.

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of anions, $\bar{\zeta}$, has been subtracted from both b and q in order to compare the oxynitrides and the oxyhalides.

We have included the charges and the bond strength sums for 78 crystallographically independent anion sites. They correspond to 28 compounds representing different structural types of oxynitrides and oxyhalides. The selection of the compounds has been performed considering as criteria the existence of cation order, the diversity of anions and structural types, and the quality of the structure determination. For instance, for oxynitrides we have chosen crystal structures determined using either neutron powder diffraction or by single-crystal X-ray diffraction, where crystallographic differentiation between oxygen and nitrogen atoms was additionally supported, in some cases, by lattice energy calculations. In this plot as in Table 1, it can be seen that there is a good correlation between b and q. Although there is a significant spread of data around the ideal correlation, the general conclusion is that regardless the structural type and the cations involved, when ordering takes place the more charged anions occupy the sites with the larger PSCR sums. The root-mean-square deviation (rms) in $(q - b)$ are 0.26 (overall), 0.20 (oxynitrides), and 0.38 (oxychlorides). On the basis of the set of structures in this study, PSCR predicts anion distributions to a typical accuracy of 20−25% for oxynitrides and oxyfluorides but only 38% for oxychlorides. This allows the a priori prediction of the anion distributions in mixed systems with different charge of anions, in a general and simple way, and just from the knowledge of the topology and the available coordination sites of anions. For instance, the predicted anion distribution for the new solid solution $Sr_{2-x}La_xNbO_{4-y}N_y$ with K_2NiF_4 structure is similar to that previously reported for the lanthanum-free compound $Sr_2NbO_{3.28}N_{0.72}$[16] (see Table 1). The bond strength sum for the equatorial anion site in $Sr_{2-x}La_xNbO_{4-y}N_y$ is larger than for the axial one for $0 \leq x \leq 1$. For example, in the hypothetical compound $La_2Nb^{V}ON_3$, b_{axial} and $b_{equatorial}$ are 2.5 and 3.0, respectively, and consequently, oxygen would preferentially occupy the axial position. We have prepared the member with $x = 0.15$ and have investigated the anion ordering by Rietveld refinement of neutron powder diffraction data. The refined stoichiometry is $Sr_{1.85}La_{0.15}NbO_{3.22}N_{0.78}$ with $b_{axial} = 1.92$ and $b_{equatorial} = 2.47$, and nitrogen is ordered, as predicted, in the equatorial sites.[26]

For oxychlorides and oxybromides, size effects and polarization also have to be considered as affecting the stabilization of a given ordered structure. In ternary oxynitrides, the satisfying of PSCR results in the tendency of nitride to coordinate a higher number of cations with respect to oxygen, as is illustrated for instance with Ge_2N_2O or TaON. Both compounds are ordered and show two crystallographically independent sites for anions. In agreement with PSCR, nitrogen and oxygen occupy respectively, the sites with CN = 3 ($b = 3$) and CN = 2 ($b = 2$) in Ge_2N_2O[27] and the sites with CN = 4 ($b = 2.86$) and CN = 3 ($b = 2.14$) in TaON.[28] In quaternary oxynitrides, the satisfying of PSCR leads to a preferred coordination of nitrogen with the more charged cation, as for instance in $Sr_4Ga_3N_3O$.[20] This ordered compound shows three sites with CN = 7 for anions; oxygen occupies a position coordinated to seven strontium atoms with $b = 2.33$, whereas two nitrogen atoms are bonded in the remaining seven coordinated sites to six strontium atoms and one gallium atom, resulting in $b = 3$. For quaternary compounds of cations with the same charge, as for instance Ba_3ZnN_2O,[29] this trend results in a preferred coordination of the transition metal with nitrogen. As the coordination number of the zinc atom in this compound is lower than for barium, b for the nitrogen site is higher than for oxygen, which is coordinated only with barium atoms ($b(N) = 2.93$ and $b(O) = 2.13$). In oxyhalides PSCR also is able to predict the anion distribution. As can be seen in Table 1, the halide always occupies the site with lower b's although the differences with the b's of oxygen sites are not so large as for N in oxynitrides. This is reflected in a larger dispersion of points for the oxyhalides in the plot of Figure 1.

We must point out that although bond valence sums (BVSs)[18] are generally more precise to interpret anion coordination preferences and would have led to similar conclusions, they need a previous knowledge of the crystal coordinates and hence cannot be used with the simplicity, as well as with the predictive character of PSCR sums that only request knowing the structural type and the available sites and coordination numbers for anions and cations.

As conclusion, this study has shown that PSCR gives a good a priori estimate of anions distributions to an accuracy of 20% at best. A comparison of this with a similar survey of anion distributions using a posteriori methods such the bond valence and energy calculations deserves certainly further attention.

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Supporting Information Available: A full table with the list of parameters represented in Figure 1 and the reference corresponding to each compound. A color version of Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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