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Introduction of a Tolerance Factor for the Nd_2CuO_4 (T')-Type Structure

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A tolerance factor, $tf = [3\sqrt{2}r_0 + 2\sqrt{6}(r_A + r_0)]/9(r_B + r_0)$, has been established for the Nd_2CuO_4-type structure, where r_A, r_B, and r_0 are the radii of the A, B, and O ions, respectively. It is based on the geometrical matching between the A–O, B–O, and O–O bond distances, and it can be used to distinguish between Nd_2CuO_4 (T')-, T^*-, and K_2NiF_4 (T)-type phases. Using Shannon's ionic radii, it is found that the T' phases occur for $tf < 1.00$ while T phases form for $tf > 1.00$. As expected, the T^* structure exists in a very narrow region between the stability boundaries of these two structure types. The fact that T' and T separate at $tf = 1.00$ suggests that the new tolerance factor model is applicable to both structure types.

INTRODUCTION

The discovery of the superconductivity in the T-type $(La, Ba)_2CuO_4$ and T'-type $(Nd, Ce)_2CuO_4$ has motivated study of crystal chemistry and physical properties of the cuprates having these structures (1, 2). The T (K_2NiF_4) structure of the ternary oxides A_2BO_4 can be described as an intergrowth of ABO_3 perovskite- and AO rock-salt layers along the c-axis, containing corner-shared BO_6 octahedra and AO_9 polyhedra. In contrast, the T' (Nd_2CuO_4) structure is derived from an intergrowth of BO_2 infinite layer sheets and A_2O_2 fluorite-type layers along the c-axis, containing corner-shared BO_4 square planes and AO_8 cubes. Although the cation arrangements in both the T'- and T-type structures are the same, their anion configurations are different. The T^* structure consists of a hybrid of the T and T' structures (3). The structure of the T'-type Nd_2CuO_4 is presented in Fig. 1.

Several research groups recently have investigated the stability of the T and T' structural types using the well-known Goldschmidt tolerance factor t as a criterion. This tolerance factor (also called the perovskite tolerance factor) is based on an analysis of the perovskite subcell of the structure and is defined as

$$t = (r_A + r_O)/\sqrt{2}(r_B + r_O), \quad [1]$$

where r_A, r_B, and r_O are the radii of the A, B, and O ions, respectively (4–8). It was found that phases with the T-type structure fall in the range $0.87 < t < 0.99$ while those with the T'-type exist for $0.83 < t < 0.86$ (5). If the phases Ln_2CuO_4 (Ln = Dy, Ho, Er, Tm, Y), prepared under high pressure (9), are included, the lower limit of t for the T' phases extends to 0.81. The T^* phases occur at tolerance factors between t of the T and T' phases.

The Goldschmidt tolerance factor provides an excellent guide for predicting when perovskite-related structures may be expected, and for classifying the structural type of compounds with the general formula ABX_3, and it has been in use for over half a century. The tolerance factor is based on the geometrical matching between the A–X and B–X layers in the cubic perovskite structure. However, the A atom is in twelve-coordination for the perovskite structure but in nine-coordination for the T-type structure. In fact, the A–O bond in the T-type structure exhibits features of both the twelve-coordination of perovskite and the six-coordination of rock salt. Perhaps for these reasons, most t values for the T phases are closer to the lower t limit (4, 5). In addition, the structure of the T^*-type $CaSmCuO_3Cl$ has been determined by single crystal X-ray diffraction (10). Unfortunately, its t value (0.842) is near the center of the T' field. In order to address these issues, we introduce a Nd_2CuO_4-type tolerance factor tf, based on the geometrical matching between the A–O, B–O, and O–O distances.

MODEL OF THE T'-TYPE TOLERANCE FACTOR tf

We assume that the AO_8 cube has an idea CsCl-type structure in the T' phase and that all ions are spherical with rigid contact to each other. The edge length L_c of the cube can be expressed as

$$L_c = a_{A-O}/\sqrt{2} \quad [2]$$

and

$$L_c = 2(r_A + r_O)/\sqrt{3}. \quad [3]$$

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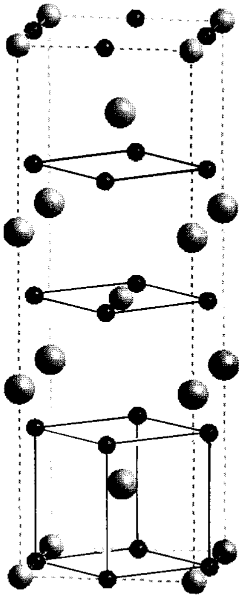

FIG. 1. Structure of the T'-type Nd_2CuO_4. Large, medium, and small balls represent Nd, Cu, and O atoms, respectively.

Substituting Eq. [2] into [3], the relationship between the a lattice parameter and the bond distances can be written as

$$a_{A\text{–}O} = 2\sqrt{6}(r_A + r_O)/3. \qquad [4]$$

In addition,

$$a_{B\text{–}O} = 2(r_B + r_O) \qquad [5]$$

and

$$a_{O\text{–}O} = \sqrt{2}(r_O + r_O) = 2\sqrt{2}r_O, \qquad [6]$$

where $a_{A\text{–}O}$, $a_{B\text{–}O}$, and $a_{O\text{–}O}$ are the a lattice parameters for equilibrium A–O, B–O, and O–O bond distances, respectively. r_A is the radius of the eight-coordinated cation, r_B is radius of the square-planar-coordinated cation, and r_O is the radius of the six-coordinated oxygen ion.

From Shannon's ionic radii (11), the a lattice parameter $a_{A\text{–}O} = 2\sqrt{6}(r_A + r_O)/3$ for the T'-type Nd_2CuO_4 is 10.7% greater than $a(T)_{A\text{–}O} = \sqrt{2}(r_A + r_O)$ for the T-type La_2CuO_4, where $a(T)_{A\text{–}O}$ is the a parameter based upon the A–O distance for the T-type structure and r_A is the radius of the nine-coordinated La^{+3}. The real difference between a of Nd_2CuO_4 and a of La_2CuO_4 is only 3.6% (12). The geometrical matching can be reached by expanding the B–O layers and elongating the AO_8 cubes along the c-axis. As a result, the O–O distance is only 279 pm in the (004) planes but 304 pm along the c-axis for Nd_2CuO_4. As the size of A decreases, the electrostatic repulsion between the coplanar oxygens in the fluorite layers increases. Based on the consideration of the competition between the A–O attraction and O–O repulsion, as well as the geometrical matching between the bond distances, a tolerance factor tf for the Nd_2CuO_4 (T')-type structure is proposed as

$$tf = [1/3\, a_{O\text{–}O} + 2/3\, a_{A\text{–}O}]/a_{B\text{–}O}. \qquad [7]$$

The weighting of factors in the numerator reflects the fact that the number of A–O bonds is twice the number of the O–O bonds in the (004) planes in the unit cell. Substituting Eqs. [4], [5], and [6] into [7], tf can be expressed as

$$tf = [3\sqrt{2}r_O + 2\sqrt{6}(r_A + r_O)]/9(r_B + r_O) \qquad [8]$$

or

$$tf = [(3\sqrt{2} + 2\sqrt{6})r_O + 2\sqrt{6}r_A]/9(r_B + r_O). \qquad [9]$$

TEST OF THE TOLERANCE FACTOR *tf*

The T' tolerance factor tf values for the T'-, T^*-, and T-type $A_2\mathrm{BO}_4$ were calculated by employing Shannon's ionic radii (11). The $A_2\mathrm{BO}_4$ phases, studied by Bringley *et al.* for their stability limits using the perovskite-type tolerance factor t (5), were selected for the test of tf. However, the T phases, for which the r_B values are not available in Ref. (11), were not included. Since these phases have the t values between 0.915 and 0.976, excluding them would not affect the determination of the stability limit of the T phases. $La_{1.5}Nd_{0.5}CuO_4$ was also rejected because the T' phase at this composition has been reported to be thermodynamically different from the T' phase at lower La concentration (6, 7). The T'-type Ln_2CuO_4 (Ln = Dy, Ho, Er, Tm, Y) and La_2PdO_4 and the T-type Ca_2GeO_4 and Sr_2VO_4 were included in the analysis (9, 13–15). The latter two adopt more than one structural type (16).

Since the four-coordinated radius of V^{+4} is not available in Ref. (11), the average V^{+4}–O bond distance (180.5 pm) of the K_2SO_4-type S_2VO_4 was taken (16). For the same reason, the Cu^{+3}–O bond distance (183 pm) found in the $NaCuO_2$ phase was used for $LaSrCuO_4$ (17). Comparison of the tolerance factors tf and t for A_2BO_4 are summarized in Table 1.

RESULTS AND DISCUSSION

This study shows that the T' phases exhibit tolerance factors in the range $1.00 > tf > 0.96$ while the T phases occur for $1.00 < tf < 1.14$. The T^* phases, as expected, exist in a very narrow region between the T and T' boundaries. A high temperature phase transition from the K_2SO_4- to T-type was found in Sr_2VO_4 (15, 16). Its $tf = 1.131$ value is near the high limit of the T phases, suggesting the region

TABLE 1
Comparison of the Tolerance Factors *tf* and *t* for the A_2BO_4 Compounds

A_2	B	tf	t	A_2	B	tf	t
T-type (A_2BO_4)							
Sr_2	Mn	1.141	0.993	Sr_2	V	1.131	0.968[b]
LaSr	Al	1.126	0.973	Sr_2	Ti	1.122	0.956
LaSr	Cu	1.101	0.971	Ca_2	Mn	1.098	0.945
Ca_2	Ge	1.098	0.945[a]	LaSr	Ga	1.077	0.932
PrSr	Fe	1.061	0.914	GdSr	Fe	1.051	0.902
Sr_2	Sn	1.047	0.917	Ba_2	Pb	1.039	0.933
La_2	Ni	1.019	0.885	$La_{1.9}Sr_{0.1}$	Cu	1.014	0.879
Pr_2	Ni	1.010	0.873*c*	La_2	Cu	1.009	0.868[c]
Nd_2	Ni	1.005	0.867[c]	La_2	Co	1.004	0.865[c]
T'-type (A_2BO_4)							
Pr_2	Cu	0.999	0.856	Nd_2	Cu	0.995	0.851
$Nd_{1.85}Ce_{0.15}$	Cu	0.991	0.847	Sm_2	Cu	0.986	0.841
Eu_2	Cu	0.983	0.837	Gd_2	Cu	0.979	0.832
La_2	Pd	0.974	0.818	Dy_2	Cu	0.972	0.824[a]
Y_2	Cu	0.970	0.822[a]	Ho_2	Cu	0.969	0.821[a]
Er_2	Cu	0.966	0.817[a]	Tm_2	Cu	0.963	0.814[a]

A_2	tf	t	A_2	tf	t
T^*-type (A_2CuO_4)					
$La_{0.85}Eu_{0.9}Sr_{0.25}$	1.001	0.859	$LaGd_{0.8}Sr_{0.2}$	1.000	0.857
$La_{0.8}SmSr_{0.2}$	1.000	0.858	$La_{0.75}SmSr_{0.25}$	1.000	0.858
$La_{0.82}SmSr_{0.18}$	1.000	0.857	$La_{1.1}Eu_{0.8}Sr_{0.1}$	1.000	0.857
$La_{0.9}Eu_{0.9}Sr_{0.2}$	1.000	0.857	$La_{0.8}EuSr_{0.2}$	0.999	0.856
$La_{1.3}Tb_{0.7}$	0.999	0.855	$La_{1.4}Tb_{0.6}$	0.999	0.856
$La_{0.9}Y_{0.8}Sr_{0.3}$	0.997	0.855	$LaDy_{0.8}Sr_{0.2}$	0.997	0.854
$LaEu_{0.9}Sr_{0.1}$	0.997	0.855	$La_{1.2}Dy_{0.8}$	0.994	0.851

[a] High pressure form.
[b] High temperature form.
[c] Orthorhombic.

with *tf* greater than this value could belong to the K_2SO_4-type field, except that of (1.141) for Sr_2MnO_4. The result of the computation of the *tf* values for the K_2SO_4-type phases Ca_2SiO_4, Sr_2MO_4 (M = Si, Ge), and Ba_2MO_4 (M = Ti, Ge, V) confirms the expectation (18).

Besides temperature, pressure also greatly affects the stability limit of the T' and T phases. For example, a high pressure phase transition from olivine-type, having six-coordinated A and four-coordinated B, to T-type was found in Ca_2GeO_4 (14). In addition, the T' phases Ln_2CuO_4 (Ln = Dy, Ho, Er, Tm, Y) with $tf \leq 0.972$ can only be prepared at high pressure due to the presence of the small size of Ln (9). Both examples follow a general rule that the coordination number of the cation increases with pressure.

The *tf* value for the T^*-type $CaSmCuO_3Cl$ is 0.993 (10). The result is better than that of t = 0.842 calculated by the perovskite tolerance factor as mentioned earlier. The tolerance factor *tf* also can be applied to the T-type halides and sulfides (19, 20). For example, the *tf* values for K_2NiF_4 (1.121), K_2CuF_4 (1.109), Ba_2HfS_4 (1.064), and Ba_2ZrS_4 (1.060) all fall in the predicted field.

CONCLUSIONS

A new tolerance factor *tf* for the Nd_2CuO_4-type structure has been proposed based on the geometrical matching between the A–O, B–O, and O–O bond distances. It has been successfully applied in the investigation of the structural stability of the T', T, and T^* phases. Surprisingly, the T and T' phases are perfectly separated by an "ideal" tolerance factor tf = 1.00, suggesting that the model relates accurately to the ionic packing factors of the T' and T structures, and clearly showing that *tf* is a very powerful classification parameter.

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