

Alternate Distortion Modes and Stability Ranges in $A_{1/2}B^{IV}O_4$ Solid Solutions Possessing the K_2NiF_4 Structure Type: A New Structural Modification of the T Phase

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Six solid solutions of formula $(A_{1-x}A'_x)_2(B_{1-x}B'_x)O_4$ have been prepared where A and $A' = Ba, Sr$; B and $B' = Ti, Sn, Pb$ in different combinations to investigate the distortion modes and stability ranges in the K_2NiF_4 (T) structure types. These series illustrate that distortions along the a -axis is dominated by the B site ion, whereas distortions along the c -axis are governed by the A site ion which contrasts the behavior of the RE_2CuO_4 phases possessing the T' structure type. The $(Sr_{1-x}Ba_x)_2PbO_4$ and $Sr_2Sn_{1-x}Pb_xO_4$ systems yielded T structure tolerance factors (t_{lim}) of 0.91 at $x = 0.5$, and 0.89 at $x = 0.75$, respectively, before a transformation to the Sr_2PbO_4 structure type. A new lower symmetry ($P4/mmm$) modification of the T phase was found for $Sr_2Sn_{1-x}Pb_xO_4$ ($0.5 < x \leq 0.75$) which has partially ordered Pb and Sn atoms on the B sites. A Reitveld refinement of $Sr_2Sn_{0.25}Pb_{0.75}O_4$ yielded the following parameters: 25°C, space group $P4/mmm$, $a = 4.1769$ (2) Å, $c = 12.591$ (1) Å, $V = 219.67$ (4) Å³, $\rho = 6.415$ (3) g/cm³, $R = 9.32\%$, $R_{wp} = 11.21\%$, and $R_{bragg} = 8.4\%$. This structure represents an alternate distortion mode for stressed K_2NiF_4 phases with mixed B site atoms. © 1992 Academic Press, Inc.

Introduction

The rare earth copper oxide phases of formula RE_2CuO_4 are known to exist in five different structural modifications, the T' (Nd_2CuO_4), T*, T'', and tetragonal and orthorhombic T (K_2NiF_4) phases (1, 2), whereas only the T phases are observed for the noncopper compounds (3, 4). Recent studies on the RE_2CuO_4 systems have shown that the range of K_2NiF_4 stability and the specific structural modifications correlate exceedingly well with the average size of the A site rare earth ion and the value of the perovskite tolerance factor t defined as

$t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$. The experiments suggest that the crystal chemistry is dominated by the composition and bonding in the A-O layers (2). The T structure contains 9-coordinate A site ions in double rock salt layers which separate the sheets of octahedral B site ions. When a reasonable match between the A-O layers and B-O layers exists ($0.99 \geq t \geq 0.88$), the T phase is tetragonal with $I4/mmm$ crystal symmetry. In many cases, an orthorhombic distortion is observed when the A-O distances become small relative to the B-O distances ($0.88 \geq t \geq 0.87$), signaling T phase instability (e.g., La_2CuO_4). Larger discrepancies in A-O/B-O distances resulting from small A ions ($t \leq 0.865$) affect structural changes to the

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T' (or T*) phase (e.g., Nd₂CuO₄). The T' phase comprises square planar CuO₂ sheets separated by fluorite-like AO layers. The A site atoms are 8-coordinate in the fluorite layers (vs 9-coordinate rock salt) which better stabilizes the smaller rare earth ions (2, 4).

There is current interest in preparing new, copper-free superconducting oxides of the early transition metals and main group elements (5–9). One strategy involves the preparation of structural analogs of the high *T_c* copper oxide phases that incorporate early transition metals with varying electronic configurations and carrier concentrations. Because of the diversity in structure and properties observed in the K₂NiF₄-type copper oxides, we and others have focused considerable attention on the preparation of reduced early transition metal complexes with this structure (10–13).

Several early transition metal oxides are known to adopt the K₂NiF₄ structure type (3) but, unlike the copper oxides, these phases are not as amenable to A site doping and changes in oxidation states. The exception is the RE–Sr–V–O system in which the Sr_{2–x}RE_xVO₄ (V³⁺–V⁴⁺) and Sr_{*n*+1}V_{*n*}O_{3*n*+1} series are known (5). Attempts to prepare reduced K₂NiF₄-type titanates (La_{2–x}Sr_{*x*}TiO₄) invariably leads to multiphase samples with significant concentrations of the reduced perovskites (12–14). Ba₂PbO₄ also adopts the T structure but is also resistant to rare earth doping (14, 15). During the attempted preparation of the afore mentioned materials, we observed some fully oxidized side products that showed changes in cell dimensions differing from those reported for the copper oxides. In this paper we describe the preparation and crystal chemistry of six solid solutions involving A and B site substitutions in T phase A₂BO₄ oxides incorporating A²⁺ and B⁴⁺ ions. Particular attention was focused on materials that approached the “edge of instability,” where cell distortions and phase transitions

are observed in the RE₂CuO₄ systems. A new, lower symmetry tetragonal form of the T structure is described for Sr₂Sn_{0.25}Pb_{0.75}O₄ that contains partially ordered Sn⁴⁺ and Pb⁴⁺ ions.

Experimental

All compounds were prepared by firing intimately ground, stoichiometric mixtures of alkaline earth carbonates and metal dioxides (Cerac Inorganics) in air at 800°C for 12 hr. The resulting powders were reground and refired according to the following schedules: (Sr_{1–x}Ba_{*x*})₂SnO₄—1300°C for 24 hr; (Sr_{1–x}Ba_{*x*})₂PbO₄—950°C for 24 hr; Sr₂Ti_{1–x}Sn_{*x*}O₄—1300°C for 24 hr; Ba₂Sn_{1–x}Pb_{*x*}O₄—1000°C for 24 hr; (Sr_{1–x}Ba_{*x*})₂Sn_{1–x}Pb_{*x*}O₄—1000°C for 24 hr; Sr₂Sn_{1–x}Pb_{*x*}O₄—950–1050°C for 24 hr. Intermediate regrindings and refrings were sometimes necessary. Significant quantities of Sr₂PbO₄ were initially formed in reactions involving Sr and Pb. The Pb-containing samples often contained traces (<5%) of lead oxide impurities and readily disproportionated at high temperatures (>1100°C) to give perovskites and other unidentified phases. The remaining samples were single-phase materials.

Samples were characterized by powder X-ray diffraction (XRD). XRD data were collected at 25°C on a modified Philips XRG 2000 diffractometer (CuK α radiation) interfaced with a RADIX data box and MDI software system. Cell refinement calculations were performed on all data collected at 20° ≤ 2 θ ≤ 70° which were corrected for sample displacement and zero point error (16). In many cases, it was necessary to perform Rietveld analyses to refine cell constants due to peak reading difficulties associated with overlapping reflections. For comparative purposes, the percentage changes in the lattice parameters of the (Sr_{1–x}Ba_{*x*})₂PbO₄ solid solution were calculated from extrapolated lattice constants of the hypo-

TABLE I
SUMMARY OF CRYSTALLOGRAPHIC DATA FOR
 $\text{Sr}_2\text{Sn}_{0.25}\text{Pb}_{0.75}\text{O}_4$

Formula	$\text{Sr}_2\text{Sn}_{0.25}\text{Pb}_{0.75}\text{O}_4$
Space group	$P4/mmm$
a (Å)	4.1769(2)
c (Å)	12.591(1)
Volume (Å ³)	219.67(4)
Density (g/cm ³)	6.415(3)
R (%)	9.32
R_{wp} (%)	11.21
R_{bragg} (%)	8.40

Note. $R = \{[\sum_i(I_i^{\text{obs}} - I_i^{\text{calc}})^2]/[\sum_i(I_i^{\text{obs}})^2]\}^{1/2}$. $R_{wp} = \{[\sum_i w_i(I_i^{\text{obs}} - I_i^{\text{calc}})^2]/[\sum_i w_i(I_i^{\text{obs}})^2]\}^{1/2}$. $R_{bragg} = [\sum_i |F_i^{\text{obs}} - F_i^{\text{calc}}|]/[\sum_i F_i^{\text{obs}}]$.

thetical tetragonal Sr_2PbO_4 phase possessing a T structure type.

The structure of the $\text{Sr}_2\text{Sn}_{0.25}\text{Pb}_{0.75}\text{O}_4$ phase was refined by Reitveld analysis (Micro-Riet, MDI) on a Compuadd 386 personal computer. Data were collected at 0.02° intervals with 10-sec count rates. The data were indexed and successfully refined on a primitive tetragonal cell (space group $P4/mmm$) with Pearson VII profile shape functions. Of the structural models used, the ordered model with Pb in the body center (Wyckoff d site) and a 1:1 mixture of Pb and Sn at the cell corners (Wyckoff a site) clearly gave a superior fit and lowest residuals. Other models, including a disordered structure with random distributions of Sn and Pb atoms on B sites, gave poor fits and high residuals. A summary of the crystallographic data is given in Table I.

Results

I. General

Four T phase solid solutions of formula $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{SnO}_4$, $\text{Sr}_2\text{Ti}_{1-x}\text{Sn}_x\text{O}_4$, $\text{Ba}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$, and $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ were prepared showing well-behaved, continuous changes in tetragonal lattice parameters for all values of $0 \leq x \leq 1$. Two additional

solid solutions of formula $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{PbO}_4$ and $\text{Sr}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ contained well-behaved K_2NiF_4 regions but formed biphasic mixtures beyond given values of x . Plots of the cell volume versus composition were linear for the T regions of the six series studied except for the $P4/mmm$ region of the $\text{Sr}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ system (see below).

II. A-Site Substitutions

Continuous substitution was found for $0 \leq x \leq 1$ in $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{SnO}_4$, whereas the T structure was only observed at $0.5 \leq x \leq 1$ for $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{PbO}_4$. Using the ionic radii of Shannon (17), one calculates a limiting tolerance factor, t_{lim} , of 0.91 for this system which is significantly higher than the corresponding t_{lim} values observed in the RE-Cu-O systems (2). Plots of the lattice parameters and c/a ratios versus composition for both systems are given in Fig. 1. Both series show significant elongations of the c -axes with increasing x ($M = \text{Sn}$, 5.5%; $M = \text{Pb}$, $\approx 6.2\%$) but much smaller expansions of the a -axes ($M = \text{Sn}$, 2.3%; $M = \text{Pb}$, $\approx 1.2\%$). Consequently, the c/a ratios increase linearly with x (increasing cell volume). Superstructures or symmetry changes were not observed in any of the phases in these series.

In the $(\text{Sr}_{1-x}\text{Ba}_x)\text{PbO}_4$ system, biphasic mixtures of orthorhombic $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{PbO}_4$ (the Sr_2PbO_4 structure) and the T phase are observed when $0 \leq x \leq 0.5$. It is interesting to note that the c/a ratio approaches 3.00 at the limiting composition of $x = 0.5$. The XRD profile of SrBaPbO_4 is shown in Fig. 2.

III. B-Site Substitutions

The T phase persists throughout the range $0 \leq x \leq 1$ in the $\text{Ba}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ and $\text{Sr}_2\text{Ti}_{1-x}\text{Sn}_x\text{O}_4$ solid solutions but only where $0 \leq x \leq 0.75$ in the $\text{Sr}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ system. Plots of the cell parameters and c/a ratios versus composition are shown in Fig. 3. In two of

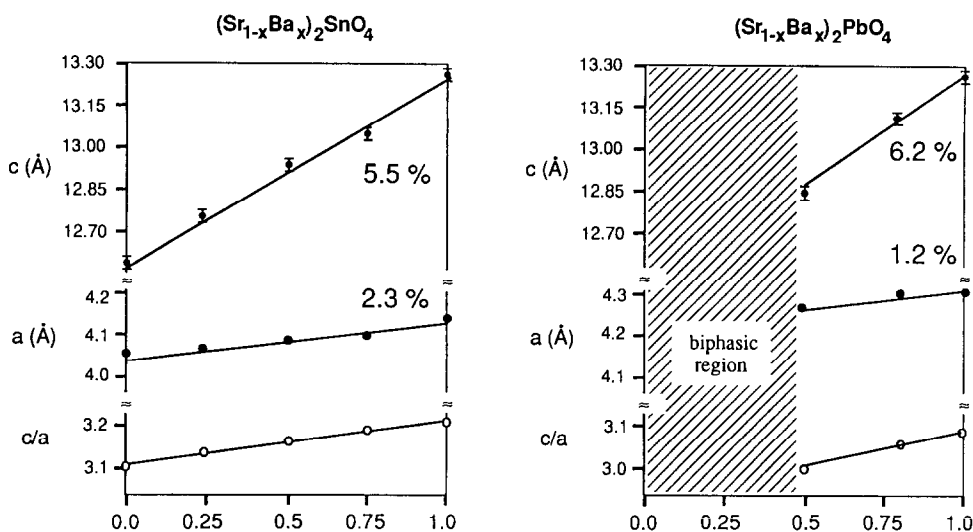


FIG. 1. Plots of cell parameters and c/a ratios as a function of composition in the (a) $(Sr_{1-x}Ba_x)_2SnO_4$ and (b) $(Sr_{1-x}Ba_x)_2PbO_4$ solid solutions.

the three series, there is a smooth decrease in the c/a ratio with increasing x (increasing volume) due to a ca. 4% elongation of the a -axes and unchanged c -parameters. For the $Sr_2Sn_{1-x}Pb_xO_4$ system, the cell parameters deviate from linearity at ca. $x = 0.5$ signaling an order-disorder transition (see below). The T phase stability region again reaches a limit at $c/a \approx 3.0$ before entering

into a biphasic region. The limiting t factor in this series is calculated to be 0.89 which is slightly higher than the corresponding t_{lim} values observed in the RE-Cu-O systems but lower than that for $SrBaPbO_4$.

At approximately $x = 0.5$, a tetragonal-to-tetragonal symmetry change takes place ($I4/mmm$ to $P4/mmm$) resulting from the ordering of the Pb and Sn atoms. The structure of $Sr_2Sn_{0.25}Pb_{0.75}O_4$ was successfully refined by using a Reitveld profile analysis (Fig. 4). The lower symmetry is evidenced by the additional reflections (arrows in Fig. 4) that are not allowed in $I4/mmm$ symmetry. A drawing of the structure is shown in Fig. 5 and a listing of the fractional coordinates and bond distances is given in Tables II and III, respectively. This phase represents a new modification of the K_2NiF_4 structure type in which the different B site ions order on nonequivalent positions in the tetragonal cell. In addition, the Sr atoms are displaced relative to the $I4/mmm$ structure such that they move along c toward the disordered Sn/Pb atoms. Slight differences in $M-O$ distances ($M = Pb$ or 50% Pb/50% Sn) are observed which are consis-

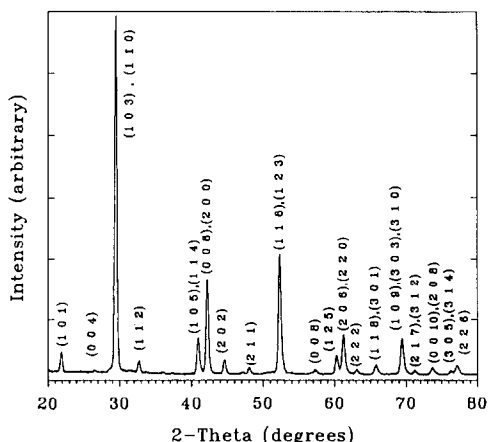


FIG. 2. Indexed XRD profile of $SrBaPbO_4$.

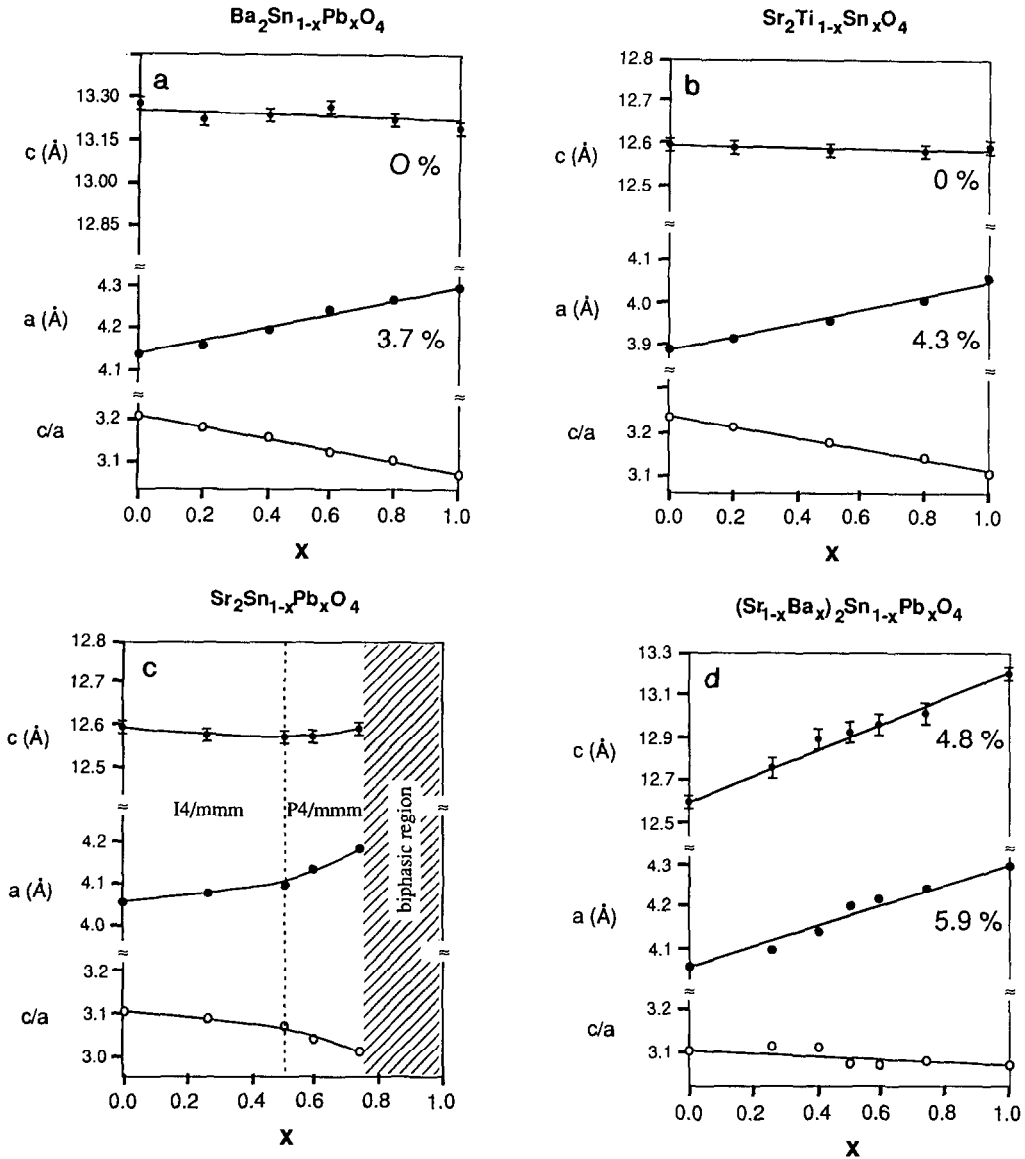


FIG. 3. Plots of cell parameters and c/a ratios as a function of composition in the (a) $\text{Ba}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$, (b) $\text{Sr}_2\text{Ti}_{1-x}\text{Sn}_x\text{O}_4$, (c) $\text{Sr}_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$, and (d) $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{Sn}_{1-x}\text{Pb}_x\text{O}_4$ solid solutions. The dashed vertical line in (c) shows the approximate boundary between the $I4/mmm$ and $P4/mmm$ regions.

tent with the differences in size of the Pb^{4+} and Sn^{4+} ions; however, oxygen positions are of course difficult to determine by this method.

IV. The $(\text{Sr}_2\text{SnO}_4)_{1-x}(\text{Ba}_2\text{PbO}_4)_x$ System

The T phase compounds Sr_2SnO_4 and Ba_2PbO_4 are mutually soluble in all propor-

tions, forming a continuous system with $0 \leq x \leq 1$. This series represents simultaneous A and B site substitution which affects large increases in both the a -parameter (5.9%) and c -parameter (4.8%) as shown in Fig. 3d. Due to the comparable increases in a and c , the c/a ratio remains essentially constant at 3.09 (1). No superstructures or symmetry changes were detected.

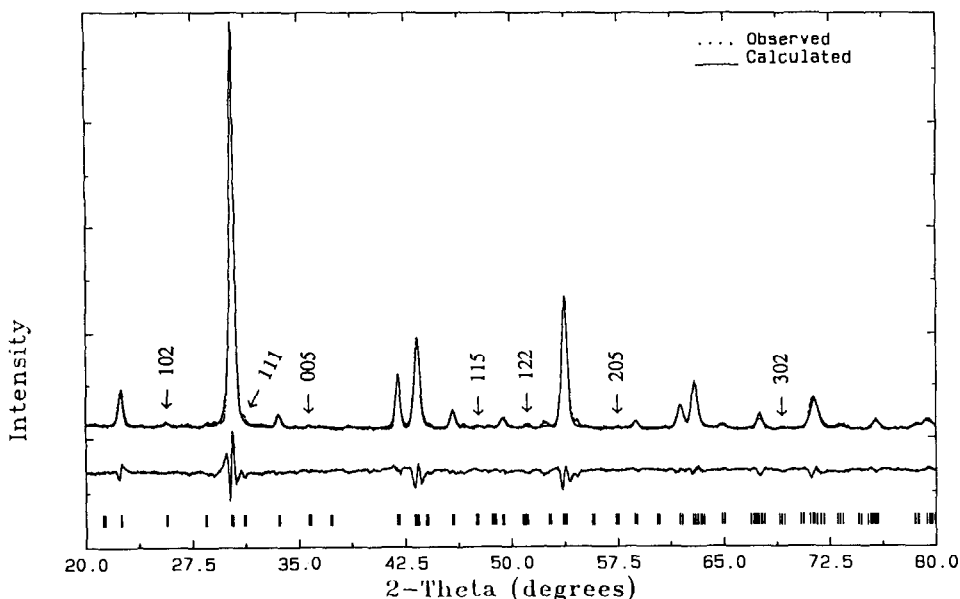


FIG. 4. Rietveld analysis results for $Sr_2Sn_{0.25}Pb_{0.75}O_4$ showing the observed (points) and calculated (solid line) profiles with the difference profile (lower line, same scale). Reflections associated with the primitive cell (absent in the $I4/mmm$ cell) are indicated with arrows. A small amount of Sr_2PbO_4 impurity is present.

Discussion

As previously discussed, the structures of the RE_2CuO_4 phases can be predicted by the perovskite tolerance factor, t (1, 2). In contrast, there are other (noncopper) oxides that fall well within the K_2NiF_4 tolerance factor stability limits ($0.87 \leq t \leq 0.99$) previously reported by Bringley *et al.* (2) but adopt different structures or do not exist [e.g., Sr_2PbO_4 , $t = 0.88$ (18), Ca_2TiO_4 , $t =$

0.91 (19)]. The T phase regions of the two Sr/Pb series reported here terminate with c/a ratios of 3.0 but have tolerance factors well within the T phase stability region of $0.99 \geq t \geq 0.87$ [$(Sr_{1-x}Ba_x)_2PbO_4$, $t = 0.91$, and $Sr_2Sn_{1-x}Pb_xO_4$, $t = 0.89$]. Thus, the tolerance factor is a useful guide for sorting the structures of some A_2BO_4 oxides but is not a ubiquitous predictor of T phase existence.

It is clear from this work and comparisons

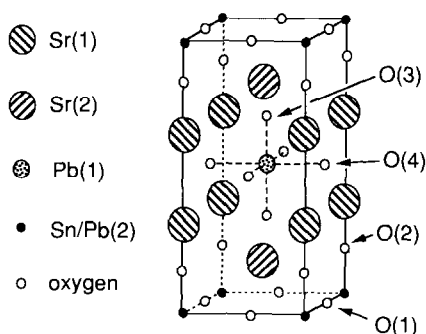


FIG. 5. Schematic drawing of the structure of $Sr_2Sn_{0.25}Pb_{0.75}O_4$.

TABLE II
FRACTIONAL COORDINATES FOR $Sr_2Sn_{0.25}Pb_{0.75}O_4$

Atom	x	y	z
Sr(1)	0	0	0.3474(8)
Sr(2)	0.5	0.5	0.1426(8)
Pb(1)	0.5	0.5	0.5
Sn/Pb(2)	0	0	0
O(1)	0	0.5	0
O(2)	0	0	0.164(5)
O(3)	0.5	0.5	0.334(5)
O(4)	0.5	0	0.5

of other known T phases (3) that the a -parameter is most significantly influenced by the radius of the B site ion, whereas the c -parameter is affected most significantly by the A site ion. These observations are consistent with the ionic B -O compression/ A -O elongation model proposed by Ganguly and Rao (4) and Poix's method of invariants (20). However, the behavior of the A_2BO_4 oxides contrasts with that of the RE_2CuO_4 -T' systems in which A site substitution affects both the a - and c -parameters equally (1, 2). Perhaps the smaller, more electropositive RE ions can polarize the "softer" Cu^{2+} center to a greater extent than the alkaline earth ions can polarize the "hard" M^{4+} ions.

The $Sr_2Sn_{1-x}Pb_xO_4$ phases with $0.5 < x \leq 0.75$ adopt a new structure type in which the Pb and Sn atoms partially order in a lower symmetry space group. Due to the weak reflections associated with the $P4/mmm$ structure, it is difficult to determine whether there is a continuous order-disorder transition occurring in this system. However, the deviations in the lattice parameters (Fig. 3c) are suggestive of a continuous phase transition of $\sim 0.5 \leq x \leq 0.75$. The $P4/mmm$ structure seems to reflect an alternate distortion mode in which A -O/ B -O mismatch ($t < 0.9$) is alleviated by allowing the small Sr^{2+} ions in the double rock salt layers to move closer

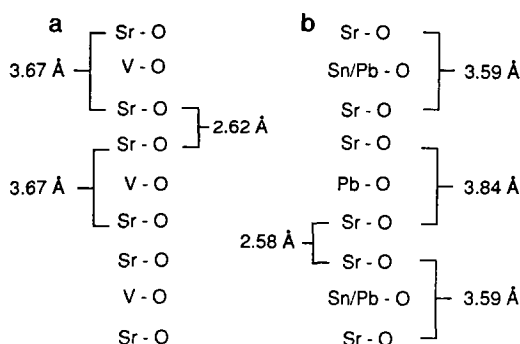


FIG. 6. Pertinent interlayer spacings in (a) Sr_2VO_4 and (b) $Sr_2Sn_{0.25}Pb_{0.75}O_4$ showing the affects of B , B' ordering. Data for Sr_2VO_4 was obtained from Ref. 21.

to the oxygens bonded to Sn. This distortion is best illustrated by comparing the interlayer spacings of $Sr_2Sn_{0.25}Pb_{0.75}O_4$ with those of Sr_2VO_4 (21) as both have very similar c -lattice parameters [for Sr_2VO_4 , $a = 3.8340(4)$ Å, $c = 12.5874(13)$ Å]. As illustrated in Fig. 6, the separations between adjacent SrO-SrO layers are quite similar in the two compounds (ca. 2.6 Å); however, the SrO-SrO gaps that host the MO_2 layers are quite asymmetric for $Sr_2Sn_{0.25}Pb_{0.75}O_4$ (Fig. 6b) in contrast to those for Sr_2VO_4 . The smaller gaps (3.59 Å) host the (Sn/Pb) O_2 layers and the larger gaps (3.84 Å) host the PbO_2 layers. Although the order-disorder transition could conceivably occur in any mixed B site system, it appears to occur only in stressed systems (low t values). This hypothesis is consistent with the absence of ordering in the $Ba_2Sn_{1-x}Pb_xO_4$ and $Sr_2Ti_{1-x}Sn_xO_4$ solid solutions in that neither series has a significant A -O/ B -O mismatch. Moreover, the differences in B site ionic radii are as large for the Sn/Ti system as for the Pb/Sn systems. A site ordering was also not detected in the $(Sr_2SnO_4)_{1-x}(Ba_2PbO_4)_x$ solid solution or $SrBaPbO_4$ even though the latter represents the limit in T phase stability with a 1:1 ratio of A site ions (e.g., a T'-related structure). Again, both series have t factors > 0.9 and instability would not be anticipated.

TABLE III
BOND DISTANCES (Å) FOR $Sr_2Sn_{0.25}Pb_{0.75}O_4$

Atoms	Distance
Pb(1)-O(3)	2.10(7)
Pb(1)-O(4)	2.0885(1)
Sn/Pb(2)-O(1)	2.0885(1)
Sn/Pb(2)-O(2)	2.07(7)
Sr(1)-O(2)	2.31(8)
Sr(1)-O(3)	2.958(4)
Sr(1)-O(4)	2.84(1)
Sr(2)-O(1)	2.75(1)
Sr(2)-O(2)	2.96(1)
Sr(2)-O(3)	2.41(1)

Superstructures have been observed in other mixed B site T phase compounds with low t values. For example, La₂Li_{0.5}Co_{0.5}O₄ ($t \approx 0.89$) shows superlattice reflections similar to those of La₂NiO₄ [supercell = $2\sqrt{a}$ unit cell (22)], whereas LaSrNi_{0.5}Ti_{0.5}O₄ ($t = 0.92$) does not (4). The superstructures of the former compounds presumably result from rotating the BO₆ octahedra about the c -axis or tilting the octahedra in the $\langle 100 \rangle$ or $\langle 110 \rangle$ directions (4). B site ordering similar to that in Sr₂Sn_{0.25}Pb_{0.75}O₄ may occur in La₂Li_{0.5}Co_{0.5}O₄ (22); however, the distortions observed in the Sr₂Sn_{1-x}Pb_xO₄ series do not involve tilting of octahedra or generation of supercells.

Conclusion

The perovskite tolerance factor has been shown to be a very useful "sorting tool" for the RE₂CuO₄ oxides but must be used more cautiously with other K₂NiF₄ metallates in describing A-O/B-O mismatches. The structure of Sr₂Sn_{0.25}Pb_{0.75}O₄ represents a new modification of the T phase representing an alternate distortion mode of mixed B site K₂NiF₄-type compounds approaching the T phase stability limit. This order-disorder transition may be useful in the design of new mixed layer copper oxide superconductors that incorporate other transition metals.

Acknowledgments

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