JOURNAL OF SOLID STATE CHEMISTRY 6, 526–531 (1973)

The Structure of La_2CuO_4 and $LaSrVO_4$*

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Received May 25, 1972

We have examined the structure of La_2CuO_4 at room temperature and found it to be an orthorhombic distortion of the K_2NiF_4 structure ($a = 5.363$ Å, $b = 5.409$ Å, $c = 13.17$ Å). Refinement of position parameters, based on powder X-ray diffraction data, shows the copper to have two long Cu–O distances (2.40 Å) and four short distances (1.90 Å). The orthorhombic unit cell becomes tetragonal at 260°C without any significant change in Cu–O distances. The magnetic susceptibility of La_2CuO_4 is less than 10^{-6} emu/g from room temperature to 4.2°K and in fields to 17 kOe. We have prepared $LaSrVO_4$ by reaction of component oxides in vacuum at 1000°C. The new compound has a tetragonal K_2NiF_4 structure with $a = 3.869$ Å and $c = 12.652$ Å. Optimization of position parameters gave two longer V–O distances (2.09 Å) and four shorter (1.94 Å).

Compounds with the general formula A_2BX_4 generally have the tetragonal K_2NiF_4 structure when the radius of the A cation is $1.0 < r_A < 1.9$ Å, the radius of the B cation is $0.5 < r_B < 1.2$ Å and X is an anion such as oxygen, fluorine or chlorine. The larger A cation has nine-fold coordination and the smaller B cation has octahedral coordination (Fig. 1). This structure can be described as containing alternate layering of perovskite (ABX_3) and rock-salt (AX) units with the nine-coordinated A cation having a surrounding that is the average of what it would be in perovskite and rock salt. This A_2BX_4 composition is one end member of a series of structurally related compounds with the general formula $AX(ABX_3)_n$ where $n = 1, 2, 3$ and ∞. As n increases, the rock salt layer is separated by a larger number of perovskite units until there are three. There are no known examples for n between 3 and ∞ (the perovskite end member).

Materials with the K_2NiF_4 structure exhibit a wide range of magnetic (*1*) and electrical properties. The investigation of these properties has given insight into the important and structurally related compounds with the perovskite structure.

As part of our broad program to investigate the properties of interesting and potentially useful transition-metal compounds, we have examined various aspects of materials with K_2NiF_4-related structures (*2*). In this paper, we report on the structure of La_2CuO_4, the effect of temperature on the structures of La_2CuO_4 and Pr_2CuO_4, and the preparation and structure of $LaSrVO_4$.

A_2CuO_4 (A = La, Pr)

Many workers (*3–7*) have reported on the preparation and characterization of Ln_2CuO_4 (Ln = La–Gd). These compounds, with the exception of La_2CuO_4, have the tetragonal K_2NiF_4 structure. The structure of La_2CuO_4 has been described as "more complex" (*3–5*) or "different" (*6*) than Ln_2CuO_4 (Ln = Pr–Gd).

We prepared La_2CuO_4 by the solid-state reaction of dried La_2O_3 and CuO. The well ground mixtures of components were fired at 1000–1200°C in air for a few days with frequent regrinding. This procedure was sufficient to yield single phase La_2CuO_4 as determined by X-ray diffraction. This same technique was used to prepare Pr_2CuO_4. After examination of the complete powder pattern for La_2CuO_4, we were able to index all diffraction peaks using an orthorhombic unit cell that is closely related to

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* This work was sponsored by the Department of the Air Force.

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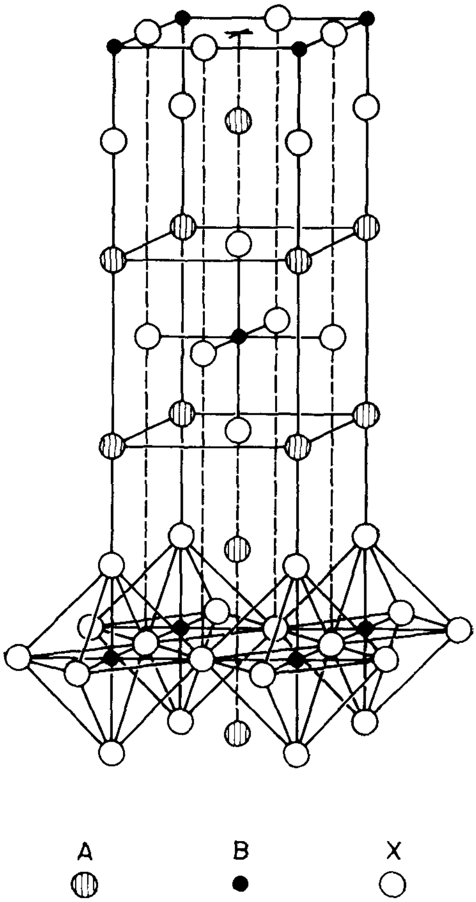

FIG. 1. The tetragonal K_2NiF_4 structure.

that of tetragonal K_2NiF_4 through the relationship:

$$a_0 \simeq \sqrt{2}\, a_T,\ b_0 \simeq \sqrt{2}\, b_T,\ c_0 \approx c_T.$$

Refinement of lattice parameters was accomplished with a computer program developed in our laboratory which minimizes the differences in observed and calculated 2θ values. Using 20 line positions as read from a slow-scanned (1/4°/min) diffractometer pattern, we obtained for La_2CuO_4

$$a = 5.363(5)\,\text{Å} \quad b = 5.409(5)\,\text{Å} \quad c = 13.17(1)\,\text{Å}$$

A similar distortion of the K_2NiF_4 structure has been found for La_2CoO_4 (*8*) and β-Na_2UO_4 (*9–11*).

In order to confirm the structure of La_2CuO_4 and determine interatomic distances, we refined the position parameters and temperature factors by minimizing the differences between our observed X-ray intensities and those calculated on the basis of an orthorhombic distortion of the tetragonal K_2NiF_4 structure. Integrated intensities for La_2CuO_4 were obtained on a General Electric XRD-5 diffractometer by accumulating both time and counts while scanning through a peak at 1/4°/min and subtracting total background as determined from a smooth plot of minimum background data. Where two or more peaks overlapped, they were grouped and assigned a single intensity value. Calculation of intensities was made assuming space group *Fmmm* and placing the atoms as given in Table I. The scattering factors for La^{3+}, Cu^{2+} (*12*) and O^{2-} (*13*) were corrected for the real and imaginary part of the anomalous dispersion term (*14*). The theoretical polarization term for a LiF-crystal diffracted-beam monochromator was also applied to our data. The two variable position parameters (z_{La} and z_{O1}) and the atomic temperature factors were refined by minimization of

$$R = 100 \times \sum |I_{\text{obsd}} - I_{\text{calcd}}| / \sum I_{\text{obsd}}$$

using a program developed in our laboratory. During the refinement based on twenty four intensities between 24° and 100° (2θ), the value of the atomic temperature factors for O1 (B_{O1}) rose to an unusually high value of 4.0.

The results of our final refinement (with $R = 2.4$) are listed in Table I and a comparison of observed and calculated intensities is given in Table II. Fixing the value of B_{O1} and B_{O2} at 1.5 changed R to 2.8 but did not change any of the variables beyond their stated error limits. Even

TABLE I

CRYSTALLOGRAPHIC DATA FOR La_2CuO_4

Unit cell dimensions:	$a = 5.363(5)^a$ Å, $b = 5.409(5)$ Å, $c = 13.17(1)$ Å
Space group:	*Fmmm* (No. 69)
Cell contents:	four La_2CuO_4; face-centered translations applied to:
La in (8*i*)	$0, 0, z; 0, 0, \bar{z}$
Cu in (4*a*)	0, 0, 0
O1 in (8*i*)	$0, 0, z; 0, 0, \bar{z}$
O2 in (8*e*)	1/4, 1/4, 0; 1/4, 1/4, 1/2
Refined parameters:	$z_{La} = 0.362(1)$, $z_{O1} = 0.182(3)$ $B_{La} = 0.7(1)$ Å^2, $B_{Cu} = 0.6(1)$ Å^2, $B_{O1} = 4(1)$ Å^2, $B_{O2} = 1.5(5)$ Å^2

[a] Value in parentheses is estimated error in last place of number.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED X-RAY DIFFRACTION DATA FOR ORTHORHOMBIC La_2CuO_4

d_{obsd}	$d_{\text{cald}}{}^a$	$h\,k\,l$	I_{cald}	I_{obsd}	d_{obsd}	d_{cald}	$h\,k\,l$	I_{cald}	I_{ob}
6.592	6.585	0 0 2	3.7	3.0^b	—	1.314	4 0 2	0.1	0.0
3.660	3.658	1 1 1	24.4	24.3	1.265	1.265	1 3 7	5.1	11.7
3.293	3.293	0 0 4	12.9	13.2	—	1.264	3 3 1	1.5	
2.876	2.877	1 1 3	100.0	100.0	1.260	1.260	3 1 7	5.1	
2.704	2.705	0 2 0	34.0	66.7	1.251	1.251	0 4 4	1.8	11.1
2.680	2.682	2 0 0	33.2		1.245	1.245	2 2 8	8.9	
2.504	2.502	0 2 2	0.7	0.8^b		1.242	4 0 4	1.8	
2.486	2.483	2 0 2	0.7	0.8^b	1.219	1.219	3 3 3	8.1	7.5
2.194	2.195	0 0 6	10.6	9.8	1.207	1.207	2 4 0	5.3	10.1
2.167	2.166	1 1 5	23.3	23.3	1.201	1.201	4 2 0	5.2	
2.090	2.090	0 2 4	15.4	30.6	—	1.188	2 4 2	0.0	2.7
2.079	2.079	2 0 4	15.2		—	1.184	0 2 10	1.1	
1.904	1.904	2 2 0	33.8	34.2	1.81	1.182	2 0 10	1.1	
1.829	1.829	2 2 2	0.5	0.4^b	—	1.182	4 2 2	0.0	
1.704	1.704	0 2 6	5.2	32.1	1.151	1.151	0 4 6	2.0	17.4
1.698	1.699	2 0 6	5.1		1.146	1.144	4 0 6	2.0	
1.695	1.695	1 3 1	3.4			1.144	3 3 5	2.4	
1.686	1.687	1 1 7	12.4		1.141	1.142	1 1 11	9.9	
1.683	1.683	3 1 1	3.3		1.133	1.134	2 4 4	4.1	8.7
1.648	1.648	2 2 4	8.3	13.6	1.128	1.128	4 2 4	4.0	
1.645	1.646	0 0 8	5.6		—	1.112	1 3 9	0.1	0.2
1.593	1.593	1 3 3	19.0	3.72	—	1.108	3 1 9	0.1	
1.583	1.583	3 1 3	18.7		—	1.098	0 0 12	0.1	0.0
1.438	1.438	2 2 6	9.3	20.1	1.082	1.083	2 2 10	1.1	1.5
1.434	1.434	1 3 5	5.5		1.058	1.058	2 4 6	2.1	10.0
1.426	1.427	3 1 5	5.4		—	1.057	1 5 1	1.0	
1.407	1.406	0 2 8	4.7	8.5	1.053	1.054	4 2 6	2.1	
1.402	1.403	2 0 8	4.6		1.052	1.052	3 3 7	3.1	
—	1.366	1 1 9	0.2	0.0^b	1.049	1.049	5 1 1	0.9	
1.352	1.352	0 4 0	5.0	4.3	1.045	1.045	0 4 8	2.6	3.0^b
1.340	1.341	4 0 0	4.8	5.0	1.039	1.040	4 0 8	2.6	3.0^b
—	1.325	0 4 2	0.1	0.0^b	1.031	1.031	1 5 3	5.1	5.0
—	1.317	0 0 10	0.4	0.0^b	1.023	1.023	5 1 3	5.0	5.8

[a] $a = 5.636$ Å, $b = 5.409$ Å, $c = 13.17$ Å.

[b] Estimated and not used in refinement.

though we have very good agreement between observed and calculated intensities, the high value of B_{01} and the poor agreement for the [400], [040], [513], and [153] reflections indicate that the true structure of La_2CuO_4 probably has symmetry lower than that required by the space group *Fmmm*. Kovba (*11*) has recently reported as a result of single crystal studies that the structure of β-Na_2UO_4 has *Pbnb* symmetry instead of *Fmmm* as earlier reported (*9*, *10*) on the basis of powder patterns.

Though some question still remains concerning the exact structure of La_2CuO_4, the general nature of the structure is not in doubt. The most striking feature of structure is the two long Cu–O1 distances (2.40 Å) and the four short Cu–O2 distances (1.90 Å). The average Cu–O distance (2.07 Å) is in good agreement with that predicted (2.08 Å) when the "effective ionic radii" of Shannon and Prewitt (*15*) are used.

If we calculate c/a_T where $a_T = (a + b)/(2 \times \sqrt{2})$, we obtain a value of 3.46. For the tetragonal K_2NiF_4 structure, c/a is always found to be 3.30 ± 0.05 (*16*) except when there is a Jahn–Teller ion present. The unusually large c/a value for La_2CuO_4 is consistent with a Jahn Teller configuration for $Cu^{2+}(d^9)$ and supports our finding of two longer and four shorter Cu–O distances.

In order to further show the structural relation of orthorhombic La_2CuO_4 to tetragonal K_2NiF_4, we have measured the lattice parameters of La_2CuO_4 as a function of temperature to 990°C using a Tempres high-temperature attachment on a General Electric XRD–5 diffractometer. The orthorhombic unit cell becomes less distorted with increasing temperature and transforms to tetragonal symmetry at 260°C. The lattice parameters for the tetragonal cell at 420°C are $a = 3.81(1)$ Å, $c = 13.24(5)$ Å; ($c/a = 3.47$). By following the position of the [006] and [200] reflections as the temperature is increased, the value of c/a was found to remain constant at 3.47 ± 0.01 up to 990°C where $a = 3.85(1)$ Å and $c = 13.37(5)$ Å. This would indicate that there is little change in going from the orthorhombic to the tetragonal unit cell. Using the pseudo-tetragonal a_T and c of the orthorhombic unit cell we are able to calculate a coefficient of linear thermal expansion (α) for La_2CuO_4 between room temperature and 990°C. The values we obtain, $\alpha_a = 12 \times 10^{-6}{}^\circ C^{-1}$ and $\alpha_c = 16 \times 10^{-6}$ $^\circ C^{-1}$, are in good agreement with those found for Sr_2TiO_4, $\alpha_a = 14.6 \times 10^{-6}{}^\circ C^{-1}$ and $\alpha_c = 14.4 \times 10^{-6}{}^\circ C^{-1}$ (*17*).

We have prepared Pr_2CuO_4 and confirm that its structure is K_2NiF_4 (*5*). Refinement of lattice parameter based on 20 line positions between 23° and 74° (2θ) gives $a = 3.966(8)$ Å, $c = 12.24(2)$ Å, and $c/a = 3.09$. This no doubt indicates that the Jahn–Teller ion Cu^{2+} has two shorter and four longer Cu–O distances. Knox (*18*) has found the same surroundings for Cu^{2+} in isostructural K_2CuF_4 ($c/a = 3.07$). These Cu–O distances are opposite to what is found for La_2CuO_4 and reflects a change from a $d^2_{x^2-y^2} - d^1_{z^2}$ (Pr_2CuO_4) to a $d^1_{x^2-y^2} - d^2_{z^2}$ (La_2CuO_4) configuration. We have followed the c/a ratio for Pr_2CuO_4 up to 900°C and find that it remains constant at 3.09 ± 0.01. At 900°C the tetragonal unit cell is $a = 4.00(1)$ Å and $c = 12.31(3)$ Å. The coefficients of linear expansion between room temperature and 900°C are $\alpha_a = 9.5 \times 10^{-6}{}^\circ C^{-1}$ and $\alpha_c = 6.7 \times 10^{-6}{}^\circ C^{-1}$. These values are much smaller than those found for La_2CuO_4.

We have investigated the magnetic properties of La_2CuO_4 using a vibrating sample magnetometer. The magnetic susceptibility of our sample (0.2142 g) was below the sensitivity of our instrument (10^{-6} emu/g) from room temperature to 4.2°K and in fields to 17 kOe. Since Cu^{2+} has an odd number of d electrons, the absence of a normal magnetic moment probably indicates antiferromagnetism.

$LaSrBO_4$

An examination of the literature (*1*) of known materials with the K_2NiF_4 structure revealed that $LaSrVO_4$ and $LaSrTiO_4$ have not been reported as members of the series $LaSrBO_4$ where B^{3+} = Al, Cr, Mn, Fe, Co, Ni, Ga, Rh. All of the known compounds have been obtained by reaction of oxides and carbonates in air, N_2 or O_2. We have attempted the preparation of $LaSrVO_4$ and $LaSrTiO_4$ by the reaction of stoichiometric amounts of dry La_2O_3, freshly prepared SrO and V_2O_3, or Ti_2O_3. The reactants were intimately mixed, pelleted and fired in evacuated silica capsules at 1000°C for 24 hr. X-ray diffraction patterns of the reaction products in the case of the Ti compound revealed a mixed phase with no compound having the K_2NiF_4 structure. However, there was compound formation for $LaSrVO_4$ with only trace amounts of a second phase.

The X-ray pattern of $LaSrVO_4$ could be interpreted assuming the material has the tetragonal K_2NiF_4 structure. Refinement of the lattice parameters was based on 15 well-defined peaks whose positions were determined from a 1/4°/min scan over the 2θ interval 50°–125°. For $LaSrVO_4$, we obtained $a = 3.869(1)$ Å and $c = 12.652(3)$ Å. The c/a ratio is 3.27 and is similar to those found for most materials wth the K_2NiF_4 structure. To confirm our structure assignment, we have compared our observed intensities with those calculated for the K_2NiF_4

TABLE III

CRYSTALLOGRAPHIC DATA FOR $LaSrVO_4$

Unit cell dimensions:	$a = 3.869(1)$[a] Å, $c = 12.652(3)$ Å (Tetragonal)
Space group:	$I4/mmm$
Unit cell contents:	two $LaSrVO_4$; body-centered translation applied to:
A in (4e)	0, 0, z; 0, 0, $\bar{z}$ where A is equal amounts of La and Sr randomly placed.
V in (2a)	0, 0, 0
O1 in (4e)	0, 0, z; 0, 0, $\bar{z}$
O2 in (4c)	0, 1/2, 0; 1/2, 0, 0
Optimized parameters:	$z_A = 0.357(2)$, $z_{O1} = 0.165(5)$, $B_{cell} = 1.0(2)$ Å^2

[a] Value in parentheses is estimated error in last place of number.

TABLE IV

COMPARISON OF OBSERVED AND CALCULATED X-RAY DIFFRACTION DATA FOR TETRAGONAL $LaSrVO_4$

d_{obsd}	d_{cald}[a]	$h\ k\ l$	I_{cald}	I_{obsd}
6.334	6.326	0 0 2	2.603	1.82
3.696	3.700	1 0 1	18.612	17.31
3.162	3.163	0 0 4	12.239	11.84
2.852	2.851	1 0 3	100.000	91.12
2.739	2.736	1 1 0	73.448	71.06
2.511	2.511	1 1 2	4.328	4.01
2.110	2.118	1 0 5	11.986	24.60
	2.109	0 0 6	14.841	
2.068	2.069	1 1 4	33.478	31.89
1.934	1.935	2 0 0	38.223	43.73
1.850	1.850	2 0 2	0.174	0.18
1.715	1.714	2 1 1	4.747	5.46
1.670	1.670	1 1 6	14.603	15.49
1.650	1.650	2 0 4	7.217	8.20
1.638	1.638	1 0 7	9.191	10.93
1.600	1.601	2 1 3	34.529	38.27
1.582	1.582	0 0 8	3.438	7.29
1.428	1.428	2 1 5	5.482	17.31
1.426	1.426	2 0 6	13.096	
1.370	1.369	1 1 8	4.441	15.52
1.369	1.368	2 2 0	10.028	
—	1.337	2 2 2	0.026	0
1.322	1.321	1 0 9	0.983	0.91
1.283	1.283	3 0 1	0.930	1.09
1.265	1.265	0 0 10	0.745	1.09
1.256	1.256	2 2 4	2.807	2.74
1.250	1.250	2 1 7	7.217	8.20
1.234	1.233	3 0 3	6.752	7.81
1.224	1.224	2 0 8	5.097	16.40
	1.224	3 1 0	9.421	
—	1.201	3 1 2	0.315	0
1.148	1.149	3 0 5	1.163	10.01
	1.148	1 1 10	3.687	
	1.148	2 2 6	5.508	
1.141	1.141	3 1 4	7.036	7.29
1.102	1.103	1 0 11	5.904	6.92
1.091	1.091	2 1 9	1.050	1.09
1.069	1.069	3 2 1	1.097	1.27
1.059	1.059	2 0 10	1.727	7.29
1.058	1.058	3 1 6	5.597	
—	1.054	0 0 12	0.035	0
1.050	1.050	3 0 7	2.133	2.74
1.040	1.040	3 2 3	7.930	8.75
1.035	1.035	2 2 8	2.912	4.19
0.9881	0.9882	3 2 5	1.476	1.45
—	0.9841	1 1 12	0.000	0
0.9676	0.9680	3 1 8	3.217	6.38
	0.9675	4 0 0	3.142	
0.9579	0.9581	2 1 11	8.386	9.11
	0.9564	4 0 2	0.003	
0.9505	0.9506	3 0 9	0.393	0.55
0.9442	0.9441	1 0 13	0.447	0.36
0.9358	0.9361	4 1 1	0.844	0.73
0.9287	0.9290	2 2 10	1.388	1.09
0.9250	0.9260	2 0 12	0.089	1.1
	0.9252	4 0 4	1.344	
0.9229	0.9229	3 2 7	3.494	3.64
0.9160	0.9162	4 1 3	6.501	6.55
0.9121	0.9122	3 3 0	2.256	2.74
0.9039	0.9039	0 0 14	1.229	1.09
—	0.9028	3 3 2	0.069	0
0.8795	0.8800	4 1 5	1.327	6.74
	0.8797	3 1 10	4.385	
	0.8794	4 0 6	3.139	
0.8763	0.8764	3 3 4	2.148	2.19
0.8652	0.8653	4 2 0	6.013	5.46
0.8547	0.8549	3 0 11	4.160	7.1
	0.8546	1 1 14	3.849	
	0.8537	4 2 2	0.004	
0.8530	0.8531	3 2 9	0.809	0.73
0.8483	0.8484	2 1 13	0.957	0.73

[a] $a = 3.869$ Å, $c = 12.652$ Å

structure in space group *I4/mmm*. In a series of calculations, we have optimized the two positional parameters (z_A and z_{O1}) and cell temperature factor (B). It was assumed that the La and Sr are randomly placed on the A site. The scattering factors for Sr^{2+}, La^{3+}, V^{3+} (*12*) and O^{2-} (*13*) were corrected for the real and imaginary parts of the anomalous dispersion term (*14*). The theoretical polarization term for a graphite crystal—diffracted beam monochromator was also applied to our data. A summary of the crystallographic data found for $LaSrVO_4$ is given in Table III. A comparison of observed and calculated intensities and d values is given in Table IV. The good agreement

$$(R = 100 \times \sum |I_o - I_c| / \sum I_o = 9.4)$$

between observed and calculated intensities confirms the assignment of the K_2NiF_4 structure to $LaSrVO_4$. Along the c axis of $LaSrVO_4$, a value of $z = 0.165$ gives two V–O1 distance of 2.09 Å while in the a–b plane, there are four

V–O2 distances of 1.94 Å. The average V–O distance in the elongated octahedron is 1.99 Å which agree exactly with that predicted from the effective ionic radii of Shannon and Prewitt (*15*).

Acknowledgments

We wish to thank Dr. J. B. Goodenough for many stimulating discussions and acknowledge the valuable technical assistance of Don Batson, Carl Anderson, and Jim Werner.

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