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Powder Diffraction Studies of the Ionic Conductor $K_{0.72}(In_{0.72}Sn_{0.28})O_2$

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The crystal structure of the sheet oxide $K_{0.72}(In_{0.72}Sn_{0.28})O_2$ has been investigated by profile analysis of a Guinier-Hägg powder diffraction record. The hexagonal unit cell has $a = 3.2314(4)$ Å, $c = 12.820(5)$ Å, $Z = 2$ and space group $P\bar{6}m2$. The structure consists of sheets of octahedra $(MO_2)_n$ (M = In,Sn) between which are inserted the potassium ions. It was found that the structure can be described as having the In and Sn atoms statistically distributed over two non-identical positions, which are 0.72 Å apart. The distribution of the potassium ions in two types of trigonal prisms has been studied. The conventional R value calculated from 32 structure factors is 0.128. Because of the limited amount of data and the statistical character of the structure, however, only the metal positions in the structure can be accurately described.

In connection with studies of ionic condustivity of new sheet phases in the KLO_2-MO_2 (L = In, Sc; M = Zr, Hf, Sn, Pb) systems,[1] structural studies of $K_{0.72}(In_{0.72}Sn_{0.28})O_2$ have been performed in order to correlate the ionic conductivity properties and the structural parameters. It has been concluded that these phases are isomorphous with the bronze $K_{0.67}CoO_2$. The potassium ions are located in trigonal prismatic sites between the $[(L,M)O_2]_n$ sheets and show a high mobility (*cf.* Fig. 1). The conductivity is better than that of β-alumina in its usual utilization range, *i.e.* above 200 °C.

Because of the equal number of electrons around In^{3+} and Sn^{4+} it was expected that the distribution of the potassium ions could be studied in a KMO_2 model of formula $K_{0.72}(In_{0.72}Sn_{0.28})O_2$. Furthermore, at room temperature the conductivity of the compound is relatively low, $5.6 \times 10^{-7} \Omega^{-1}$ cm^{-1}.

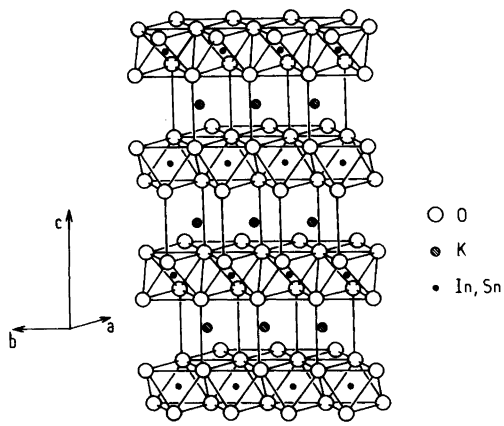

Fig. 1. The arrangement of $(In,Sn)O_6$ octahedra and KO_6 trigonal prisms in $K_{0.72}(In_{0.72}Sn_{0.28})O_2$. The potassium ions are shown in one of the two possible types of trigonal prisms.

Therefore, the potassium ions were expected to be fixed at definite positions at this temperature and in a zero electric field. Due to lack of single crystals, however, the study had to be based on powder data. Since the primary interest in this study was to obtain information about the metal atoms in the structure, X-ray rather than neutron diffraction data were collected.

EXPERIMENTAL

The sample $K_{0.72}(In_{0.72}Sn_{0.28})O_2$ used in this study was prepared and characterized in the way described in Ref. 1.

A powder diffraction photograph was taken in a focussing camera of the Guinier-Hägg type, with strictly monochromatized $CuK\alpha_1$ radiation ($\lambda = 1.54056$ Å). Silicon ($a = 5.430880(34)$ Å at 25 °C)[2] was added as an internal theta-standard. Since the sample was strongly hygroscopic it had to be protected from moisture by being sealed between two pieces of adhesive tape with low X-ray absorption coefficient. The exposure time was 1 h, and single-coated film was used so that a back-layer profile would be avoided and the background diminished, thus improving the signal-to-noise ratio. Peak positions and step-scan intensities were evaluated by an automatic film-scanner system.[3] The 2θ-step used was 0.03169° and the upper limit in 2θ was 85.7°.

From the similarities between the observed pattern and a diffraction pattern obtained from $K_{0.67}CoO_2$[4] approximate unit cell dimensions were derived. The least-squares[5] refined hexagonal cell dimensions, $a = 3.2314(4)$ Å and $c = 12.820(5)$ Å, were derived from peak positions obtained by a parabolic correction curve calculated from the positions of the internal standard lines. The observed and calculated powder pattern is given in Table 1. The correctness of the unit cell is confirmed by a de Wolff figure of merit,[6] M = 102, for the 14 strongest observed lines with indices obtained from the most closely approximating calculated theta values, thus disregarding the overlaps.

Table 1. X-Ray powder diffraction data for $K_{0.72}(In_{0.72}Sn_{0.28})O_2$. $CuK\alpha_1$ radiation ($\lambda = 1.54056$). Internal standard; Si ($a = 5.43088$ Å at 25 °C).

d_o (Å)	d_c (Å)	$h\,k\,l$	I_o
6.411	6.410	0 0 2	1588
3.204	3.205	0 0 4	406
2.7986	2.7985	1 0 0	1091
2.5643	2.5647	1 0 2	1868
2.3398	2.3411	1 0 3	235
2.1072	2.1080	1 0 4	1168
1.6992	1.6982	1 0 6	315
1.6159	1.6157	1 1 0	749
1.5669	1.5667	1 1 2	588
1.4428	1.4427	1 1 4	402
1.3994	1.3992	2 0 0	253
	1.3671	2 0 2	
1.3669	1.3669	1 1 5	381
1.2822	1.2823	2 0 4	353
	1.2820	0 0 10	
1.1703	1.1706	2 0 6	170

STRUCTURAL STUDIES

a. Indium and tin. The structure was studied by means of the Rietveld profile analysis procedure.[7] The original Rietveld program which was written for neutron diffraction data has been rewritten for Guinier data[8] and now further extended for simultaneous structure refinement of two phases present in a powder sample.[9]

Fractional atomic coordinates derived from the study of $K_{0.67}CoO_2$[4] were used as starting parameters for a number of different refinements in space group $P6_3/mmc$. It was not found possible, however, to reach any R_F $(= \Sigma|\sqrt{I_{obs}} - \sqrt{I_{calc}}|\Sigma\sqrt{I_{obs}})$ value below 0.23 using this space group. Furthermore, efforts to refine an (In,Sn)-position in the non-centric space group $P\bar{6}m2$ failed. The most notable differences between observed and calculated structure factors were found for the reflections (110), (112), (114) and (202). The calculated intensities for these reflections were always considerably less than the observed values. No changes in potassium or oxygen parameters could in any significant way reduce the R_F value. The different ionic radii for In^{3+}, 0.790 Å,[10] and Sn^{4+}, 0.690 Å,[10] made it conceivable, however, that these atoms were situated in two non-identical positions inside the oxygen octahedra, both with site position 2(*h*) in space group $P\bar{6}m2$. A least-squares profile refinement of the In and Sn positions converged at $R_F = 0.17$ with the In and Sn coordinates (1/3, 2/3, 0.244) and (1/3, 2/3, 0.301), respectively (*cf.* Table 2). Since the atomic scattering factors for In^{3+} and Sn^{4+} are almost identical it is impossible to prove from the diffraction data that In and Sn are not mixed within each of the two positions. If the two kinds of ions are assumed to be differently situated, as

Table 2. Atomic coordinates and occupancies.

Atom	Point set	x	y	z	Occupancy
In	2(h)	1/3	2/3	0.239(1)	0.72
Sn	2(h)	1/3	2/3	0.295(2)	0.28
K1	1(c)	1/3	2/3	0	0.117(8)
K2	1(d)	1/3	2/3	1/2	0.117(8)
K3	1(a)	0	0	0	0.243(8)
K4	1(f)	2/3	1/3	1/2	0.243(8)
O1	2(i)	2/3	1/3	0.108[a]	1.0
O2	2(g)	0	0	0.316[a]	1.0

[a] These parameters should not be considered as oxygen coordinates (*cf.* text).

described above, the observed occupancies correspond to the stoichiometry. A mixing also seems unlikely because of the differences in radius and charge of the ions. The obtained z-coordinate values for In^{3+} and Sn^{4+} certainly tend to decrease the electrostatic repulsion between the ions.

As was seen from the observed intensity curve no super-structure lines are present in the pattern. Thus it may also be concluded that the In and Sn atoms despite their particular positions are statistically distributed within the structure without any detectable long-range order. Furthermore, from charge considerations it may be expected that they are also statistically distributed within the $[(L,M)O_2]_n$ sheets.

b. Oxygen. Because of the limited amount of data available, it was not possible to refine the oxygen positions. The difficulties were aggrevated by the expected short-range order of the structure. The relatively large difference, 0.72 Å, along the c-axis between the two statistically occurring In^{3+} and Sn^{4+} positions should give rise to more than one oxygen position within each one of the point sets 2(*i*) and 2(*g*). Furthermore, although the potassium ions are all in special positions, having no variable positional parameter, the statistical distribution of them, as concluded from the ionic conductivity,[1] makes it extremely difficult to interpret any formally refined oxygen coordinate as a real positional parameter. Therefore, the formal "oxygen coordinates" obtained from least-squares refinements of the structure and given in Table 2, should not be regarded as simple arithmetic means of two discrete oxygen positions. It should be kept in mind that the statistical nature of all structural parameters, not only the In^{3+} and Sn^{4+}, will affect the structure factors.

c. Potassium. There are two different types of trigonal prismatic sites available for the potassium ions between the $[(In,Sn)O_2]_n$-sheets. The sites are schematically illustrated in Fig. 2. If K^+ is located in poiπt positions 1(c) or 1(d), referred to as type A below, trigonal KO_6 prisms share faces with InO_6 and/or SnO_6 octahedra. If K^+ is located in 1(a) or 1(f), called type B positions, the trigonal prisms share edges with InO_6 and/or SnO_6 octahedra. Since there is no variable positional parameter in any one of the four possible potassium sites it was thought that the statistical distribution of the ions between the two types of sites could be derived from the diffraction data.

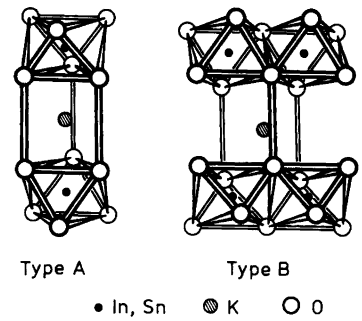

Fig. 2. Type A and B arrangements of trigonal KO_6 prisms and $(In,Sn)O_2$ octahedra in $K_{0.72}(In_{0.72}Sn_{0.28})O_2$.

With the composition of the compound fixed and the occupancies of the positions 1(c), 1(d) (type A) and 1(a), 1(f) (type B) assumed pairwise equal (*i.e.* the structure containing the same number of potassium ions of each type in each layer) a least-squares profile refinement was made. The formal "oxygen atoms" were held in average positions obtained from earlier refinements, and the refinement was considered complete when all shifts were less than 10 % of the standard deviation of the corresponding parameter. The parameters refined were the z coordinates for In and Sn, one parameter describing the distribution of the potassium ions (*i.e.* occupancy parameters with a constraint function), one isotropic over-all temperature factor, one scale factor, one asymmetry and two half-width parameters. The final R_F-value obtained was 0.128. The corresponding conventional R-value calculated from the structure was found to be identical with the R_F-value. The observed and calculated structure factors are given in Table 3. The structure factors were derived from the observed and calculated profile intensities.

The over-all temperature factor obtained was -1.6 Å^2. No physical significance, however, can be given to the negative "temperature factor" because of the strong correlations between absorption, scale factor and temperature factor.[9]

From the occupancy factor obtained it may be concluded that approximately 1/3 of the potassium ions occupy type A and 2/3 type B positions. This is also in agreement with the conclusion that the type B positions corresponding to longer In,Sn···K distances, should be more electrostatically favourable (*cf.* Fig. 2). It may also be mentioned that

Table 3. Observed and calculated structure factors obtained from least-squares profile analysis refinement of X-ray Guinier-Hägg powder diffraction data for $K_{0.72}(In_{0.72}Sn_{0.28})O_2$.

$(h\,k\,l)$	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	$(h\,k\,l)$	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$
0 0 2	63	69	1 1 4	69	71
0 0 4	71	80	2 0 0	75	68
1 0 0	80	73	2 0 1	3	4
1 0 1	9	4	1 0 8	35	36
1 0 2	81	80	2 0 2	67	72
1 0 3	32	25	1 1 5	15	16
0 0 6	66	30	2 0 3	15	19
1 0 4	77	72	1 1 6	36	29
1 0 5	7	15	2 0 4	67	66
1 0 6	62	52	0 0 10	6	6
1 1 0	117	115	1 0 9	15	18
1 1 1	1	1	2 0 5	5	13
0 0 8	46	47	1 1 7	14	9
1 1 2	77	59	2 0 6	54	49
1 0 7	19	14	1 0 10	35	26
1 1 3	12	10	1 1 8	44	45

various least-squares profile refinements using other "oxygen parameters" show no significant deviations from the remaining structural parameters given in Table 2.

In order to illustrate the sensitivity of the method used for determination of the potassium distribution a number of least-squares profile refinements with various fixed potassium occupancy parameters were carried out. The R_F values obtained with K^+ situated entirely at A or B were 0.167 and 0.263, respectively. The minimum value $R_F = 0.128$ was found for 67.5 % K^+ at B and 32.5 % at A.

DISCUSSION

The conductivity of the material is caused by a two-dimensional transport of potassium ions between the $[(In,Sn)O_2]_n$ sheets. This means that the potassium ions of the structure model illustrated in Fig. 1 must shift between the type A and B positions during the transport. As discussed above, however, the type A positions are less electrostatically favourable than the type B positions. This effect is probably enhanced if any of the neighbouring MeO_6 octahedra contain Sn^{4+} because of this ion's large deviation from the ideal position $z = 0.25$. As a consequence it seems likely that the mobility of K^+ in such type A positions is strongly reduced. This may also explain why the activation energy is as high as 0.69 eV,[1] *i.e.* why the conductivity is small at lower temperatures.

We could not find any correlation between the probability of presence of the In^{3+} and Sn^{4+} ions in the adjacent sites and the distribution of potassium between the type A and B positions. It is tempting to correlate the shift of the z-coordinates of In^{3+} and Sn^{4+} from the ideal value with the neighbourhood of the K^+ ions, but the existence of only one cobalt position in the CoO_2 sheets of the analogous metallic $K_{0.67}CoO_2$ phase seems to indicate that the driving force of the shift is not repulsion by K^+ ions, but rather the differences in charge and size of the In^{3+} and Sn^{4+} ions.

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