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Electrical Conductivity and Defect Chemistry of $PbMoO_4$ and $PbWO_4$

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The ionic and electronic conductivities of Czochralski-grown single crystals of $PbMoO_4$ and $PbWO_4$ are reported and discussed. Nominally pure crystals, as well as crystals with various aliovalent dopants, were used. From the electrical measurements it is concluded that oxygen vacancies are responsible for the ionic conductivities in both compounds. At high temperatures electronic conductivity predominates. Measurements of the oxygen partial pressure dependence of the electronic conductivity reveal that hole conduction prevails in $PbWO_4$, while mixed conduction by holes and electrons is present in $PbMoO_4$.

1. Introduction

The optical and electrical properties of scheelite-structured $PbMoO_4$ and $PbWO_4$ have received much attention in the literature (*1–10*). The photoconductivities of these compounds have been reported recently (*11*). The application of $PbMoO_4$ in acousto-optic devices (*12–15*) has promoted the growth of large, optically clear, single crystals. To date the Czochralski method has been employed to grow crystals of $PbMoO_4$ and $PbWO_4$ (*1, 4–8, 12, 13, 16*).

Since little is known about the defect chemistry of these compounds we have studied the electrical properties of undoped and doped $PbMoO_4$ and $PbWO_4$. At low and moderate temperatures ionic conductivity prevails in these compounds, while at elevated temperatures an oxygen-dependent electronic conductivity predominates, as has also been observed by van Loo (*2*).

2. Experimental

Nominally pure and doped crystals of congruently melting $PbMoO_4$ and $PbWO_4$ were grown by the Czochralski method as described by van Loo (*2*). As starting materials high-purity $PbMoO_4$ (Johnson–Matthey grade I) and high-purity $PbWO_4$ (Alpha-Inorganics) were used, and as dopants Na_2MoO_4 (Merck p.a.), K_2WO_4 (Alpha-Inorganics), Bi_2O_3 (Baker), Y_2O_3 (Fluka, A. G.), MoO_3 (Koch), and WO_3 (Koch). Single crystals doped with Na(K) were grown from a melt consisting of $PbMoO_4$ ($PbWO_4$) and equimolar proportions of Na_2MoO_4 (K_2WO_4) and MoO_3 (WO_3). Crystals doped with Bi (Y) were grown from a melt consisting of $PbMoO_4$ ($PbWO_4$), δ-Bi_2O_3 (Y_2O_3), and 2δ-MoO_3 (WO_3).

We could pull two or three practically colorless $PbMoO_4$, $PbMoO_4$:Bi, and $PbWO_4$ crystals (length 3–4 cm, diameter 0.5–1.0 cm) from each melt. The crystals grown subsequently from the same melt became increasingly yellow colored. For $PbMoO_4$:Na, $PbMoO_4$:Y, $PbWO_4$:Bi, and $PbWO_4$:Y it was not possible to obtain colorless crystals. All crystals of $PbWO_4$:K, however, were colorless.

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Electrical measurements, performed on the least-colored crystals of each type, were carried out in the temperature region 350–1200°K in air. Usually crystals were measured as grown, but in the case of $PbMoO_4$ we also used crystals annealed for 70 hr at 1250°K in a purified nitrogen or an oxygen atmosphere. Unoriented polished disks with thicknesses varying from 0.03 to 0.2 cm and surface areas of 0.1 to 0.3 cm^2 were spring-loaded between two platinum electrodes in a nickel conductivity cell, which could be evacuated. Electrical contact was achieved by means of platinum paint (Leitplatin 308A). The ionic and electronic conductivities were first measured in air, with the crystals warmed up by two steps of 50° a day from 350 to 1250°K and, subsequently, cooled down at the same speed. In this way equilibrium was established and reproducible results were obtained.

The ionic and electronic contributions to the total conductivity were obtained by means of complex admittance analysis. In the range 100 Hz to 50 kHz the admittance parameters were measured using a Wayne–Kerr autobalance bridge B641 in combination with a Rohde and Schwartz oscillator and detector SUB. In the range 0.1 to 1000 Hz admittances were measured in terms of a parallel R–C combination with a bridge in combination with a Wavetek sweepgenerator (Model 144), and a Tektronix storage scope (Type 504B) (*17*).

The electronic conductivity was also determined from current–voltage characteristics, which were measured with a Solartron digital voltmeter (Type LM 1450) and a Keithley digital picoammeter (445). The dc voltage applied to the crystal was kept under 100 mV. For small electronic contributions current–voltage characteristics yielded more reliable data.

In the temperature range 700–1200°K the electronic conductivity was measured as a function of the oxygen partial pressure. These experiments could only be performed reproducibly after the cyrstals were heated to 1200°K. Below 700°K it was also impossible to obtain reproducible results. In addition, the lower the temperature the more slowly the equilibrium was reached, irrespective of the oxygen pressure applied.

Analysis of the dopant concentrations in several crystals was performed with atomic absorption analysis and emission spectrography.

3. Results

3.1 General

The ac conductivities showed frequency dispersion in the frequency range applied: for $PbMoO_4$:Na, up to about 715°K; for undoped $PbWO_4$, up to 780°K; for $PbWO_4$:K and $PbWO_4$:Y, up to 890°K; for $PbMoO_4$:Bi, up to 1110°K; for undoped $PbMoO_4$ and $PbMoO_4$:Y, up to 1200°K; and for $PbWO_4$:Bi, up to 1250°K. Some representative admittance diagrams are given in Fig. 1. Frequency-independent

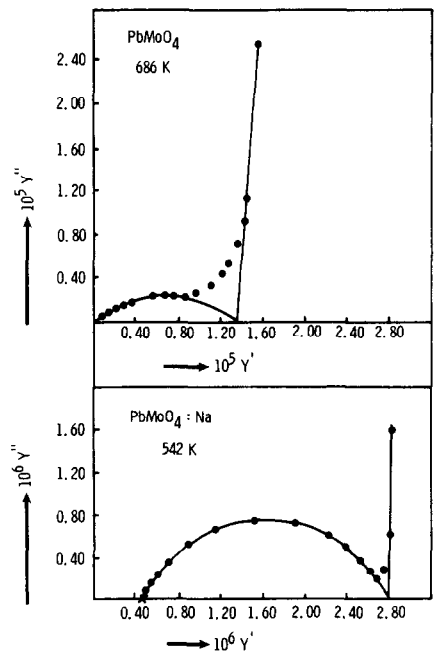

FIG. 1. Admittance plots for a nominally pure and a Na-doped $PbMoO_4$ crystal measured in air.

conductances represent true bulk properties, as was concluded from experiments on samples of different thicknesses.

The absence of frequency dispersion at higher temperatures was confirmed by the observation that direct currents showed no time dependence over the applied voltage range. Also, ac conductivities coincided with dc conductivities. These results indicate that electronic conductivity predominates at temperatures higher than those mentioned above.

3.2. Ionic conductivity

In Fig. 2 the ionic conductivities of several $PbMoO_4$ crystals are presented. One can discern two slopes corresponding to intrinsic and extrinsic conductivities.

The initial heating run of as-grown undoped crystals reveals extrinsic conductivity over the entire temperature region.

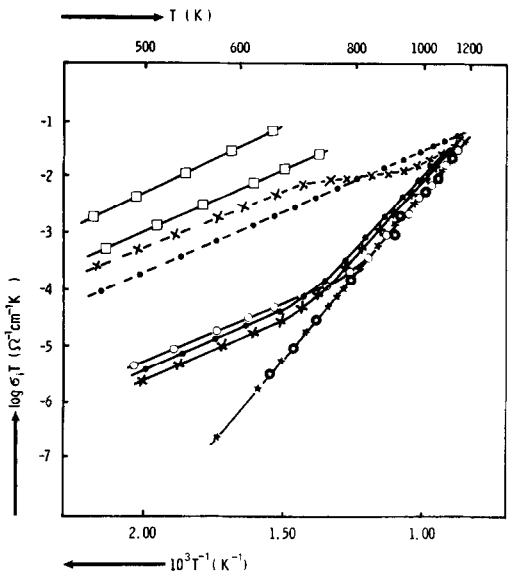

FIG. 2. The ionic conductivity σ_i of several $PbMoO_4$ single crystals plotted as $\log \sigma_i T$ versus $1/T$. (●- -●) Undoped, as-grown crystal; (●——●) undoped, equilibrated crystal; (○——○) oxygen-annealed crystal; (×- -×) nitrogen-annealed crystal, initial run; (×——×) nitrogen-annealed crystal, cooling run; (□——□) Na-doped crystals, two different Na-concentrations; (★——★) Bi-doped crystal; (✪——✪) Y-doped crystal.

Upon cooling they exhibit intrinsic conductivity at higher temperatures and extrinsic conductivity at lower temperatures which is one to two orders of magnitude smaller than that exhibited during the initial run (see Fig. 2). Upon subsequent heating reproducible conductivities were measured. The conductivity of crystals annealed in oxygen is similar to that of undoped $PbMoO_4$ on cooling. In the initial heating run the extrinsic conductivity of a crystal, annealed in nitrogen, is slightly larger than that of as-grown $PbMoO_4$. Above 740°K, however, a process starts by which the conductivity eventually equals the cooling curve of as-grown $PbMoO_4$. Crystals doped with Na or Bi show no difference between initial heating and cooling runs and exhibit only extrinsic or intrinsic conductivities, respectively. It was not possible to measure reproducibly the conductivity of $PbMoO_4$:Y crystals during the initial heating run. On cooling they exhibit only intrinsic conductivity.

In Fig. 3 the ionic conductivities of several $PbWO_4$ crystals are presented. No differences between initial and cooling runs were observed. Undoped $PbWO_4$, $PbWO_4$:K, and $PbWO_4$:Y show exclusively extrinsic conductivities, while $PbWO_4$:Bi shows only intrinsic conductivity.

3.3. Electronic Conductivity

Figure 4 shows the electronic conductivities of several equilibrated $PbMoO_4$ crystals. It was impossible to obtain reproducible results on as-grown crystals. The electronic conductivities of all equilibrated samples, except $PbMoO_4$:Na, show great resemblance. $PbMoO_4$ crystals which were equilibrated in nitrogen at 1250°K exhibit a higher electronic conductivity during the initial heating run than on cooling. At about 740°K, however, a process starts by which the conductivity eventually equals that measured on cooling.

In the temperature region 700–1200°K the electronic conductivities of several doped

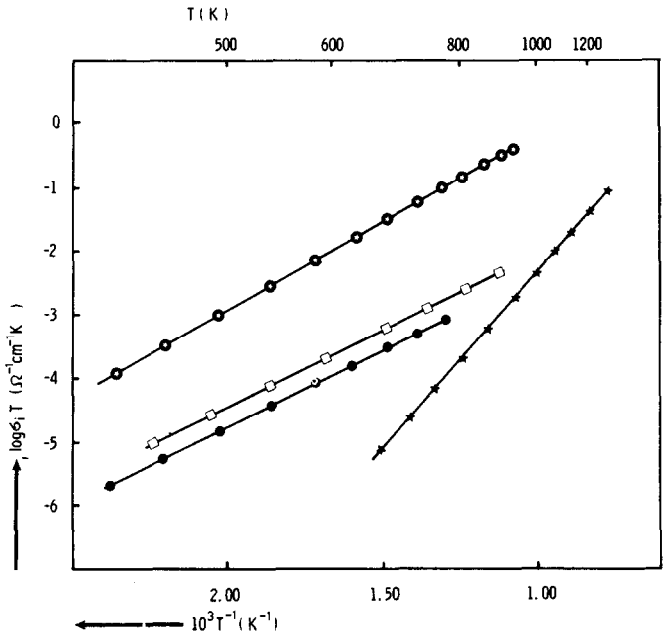

FIG. 3. The ionic conductivity of several $PbWO_4$ single crystals plotted as $\log \sigma_i T$ versus $1/T$. (●——●) Undoped crystals; (□——□) K-doped crystal; (★——★) Bi-doped crystal; (✪——✪) Y-doped crystal.

and undoped $PbMoO_4$ crystals show little dependence on the oxygen partial pressure (see Fig. 5). Up to about 880°K, no dependence on the oxygen partial pressure is found in the case of $PbMoO_4$ and $PbMoO_4$:Bi. For $PbMoO_4$:Na slopes of +0.05 at 700°K to +0.14 at 1020°K were observed in a $\log \sigma_e$ versus $\log P_{O_2}$ plot.

Figure 6 shows the electronic conductivities of several $PbWO_4$ crystals as a function of temperature. No differences were found between as-grown and equilibrated crystals. The electronic conductivities of all samples show great resemblance, viz., higher slopes at low temperatures than at high temperatures. No reproducible results could be obtained for $PbWO_4$:Y, since equilibrium with the surrounding atmosphere could not be obtained.

In Fig. 7 the oxygen partial pressure dependence of the electronic conductivities of undoped $PbWO_4$ and $PbWO_4$:K is presented.

3.4. Analysis of the crystals

The starting mixture used for the growth of doped single crystals contained 0.5 m/o (mole percentage) of dopant for Na and K, and 1.0 m/o for Bi and Y. It was not possible to grow $PbMoO_4$:Bi crystals from such a melt under our experimental conditions. Finally, crystals of $PbMoO_4$:Bi were grown from a melt containing 0.05 m/o Bi.

The results of the analysis on Na, K, Bi, and Y in several crystals are given in Table I.

4. Discussion

4.1. Defect Chemistry

To understand the conduction mechanisms and the defect chemistry of $PbMoO_4$ and $PbWO_4$, it is helpful to evaluate some internal equilibria and equilibria with the gas phase, viz.,

$$O_O^\times + V_i^\times \leftrightarrows V_O^{\cdot\cdot} + O_i'', \qquad [V_O^{\cdot\cdot}][O_i''] = K_1, \Delta H_f; \qquad (1)$$

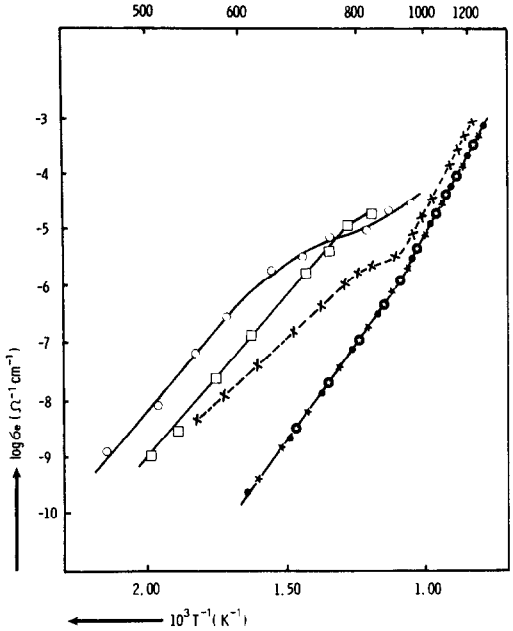

FIG. 4. The electronic conductivity σ_e of several $PbMoO_4$ single crystals plotted as log σ_e versus $1/T$. (●——●) Undoped crystals, equilibrated; (×– –×) nitrogen-annealed crystal, initial run; (○——○) Na-doped crystals, two different Na-concentrations, equilibrated; (★——★) Bi-doped crystal, equilibrated; (✪ —— ✪) Y-doped crystal, equilibrated.

$$PbO(g)+V''_{Pb}+V^{\cdot\cdot}_{O} \leftrightarrows Pb^{\times}_{Pb}+O^{\times}_{O},$$

$$a_{PbO}[V^{\cdot\cdot}_{O}][V''_{Pb}]=K_2,\ \Delta H_2; \qquad (2)$$

$$2h^{\cdot}+O^{\times}_{O} \leftrightarrows V^{\cdot\cdot}_{O}+\tfrac{1}{2}O_2,$$

$$[V^{\cdot\cdot}_{O}]P^{1/2}_{O_2}/[h^{\cdot}]^2=K_3,\ \Delta H_3; \qquad (3)$$

$$O^{\times}_{O} \leftrightarrows V^{\cdot\cdot}_{O}+2e'+\tfrac{1}{2}O_2,$$

$$[V^{\cdot\cdot}_{O}][e']^2P^{1/2}_{O_2}=K_4,\ \Delta H_4. \qquad (4)$$

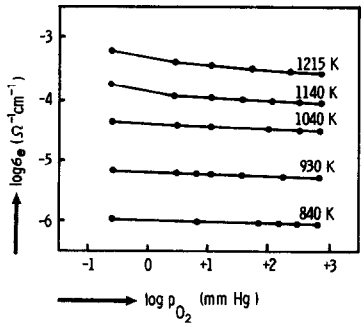

FIG. 5. The oxygen partial pressure dependence of the electronic conductivity of $PbMoO_4$.

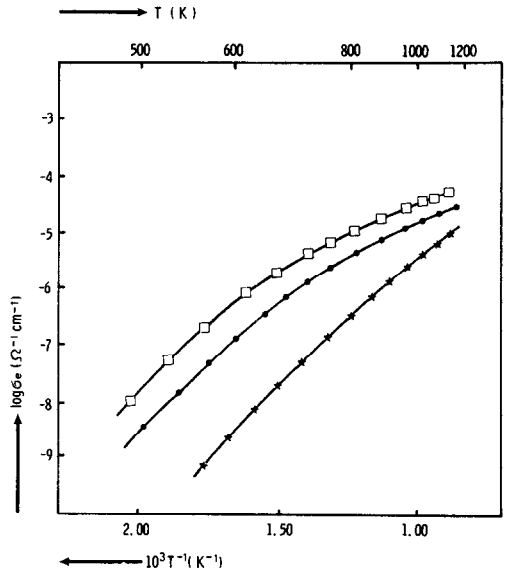

FIG. 6. The electronic conductivity σ_e of several $PbWO_4$ single crystals plotted as log σ_e versus $1/T$. (●——●) Undoped crystals; (□——□) K-doped crystal; (★——★) Bi-doped crystal.

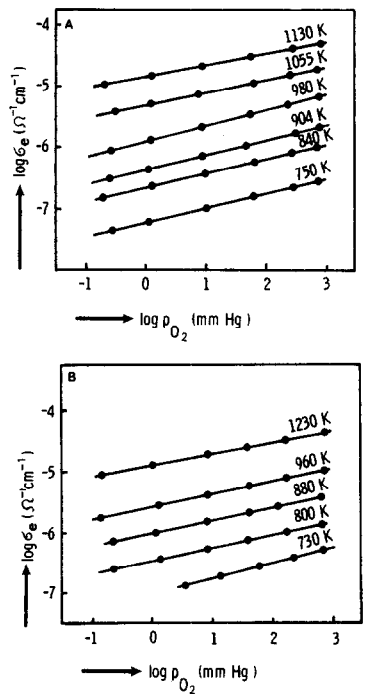

FIG. 7. The oxygen partial pressure dependence of the electronic conductivity of $PbWO_4$. (A) K-doped $PbWO_4$; (B) undoped $PbWO_4$.

TABLE I

ANALYSIS OF THE CONCENTRATIONS (MOLE PERCENTAGE) FOR DELIBERATELY ADDED DOPANTS

	$PbMoO_4$	$PbWO_4$
Na	0.5[a]	—
K	—	0.1[b]
Bi	0.01	0.4
Y	0.7	0.77

[a] Value determined for the highest Na concentration.
[b] Detection limit.

We neglect defects with high effective charge such as molybdenum interstitials or molybdenum vacancies, because these are not very likely to exist.

As Schmalzried (*18*) has pointed out, one has to take into account two independent variables in addition to pressure and temperature when dealing with ternary compounds. One can choose the oxygen partial pressure P_{O_2} and the thermodynamic activity of one of the two binary components, e.g., a_{PbO} or a_{MoO_3} (a_{WO_3}). Evaluation of the concentration dependence of some defects on the oxygen partial pressure yields the results presented in Table II (*19*).

On the basis of D.T.A. experiments van Loo (*2*) concluded that in $PbMoO_4$ ($PbWO_4$), as grown in our laboratory, an excess of MoO_3 (WO_3) is present. This deviation from molecularity leads to the electroneutrality condition

$$[V''_{Pb}] = [V^{\cdot\cdot}_{O}]. \quad (5)$$

When mono- (M^+) and trivalent (Me^{3+}) impurities on Pb^{2+} sites are present in concentrations comparable to those in Eq. (5), the electroneutrality condition reads

$$[M'_{Pb}] + 2[V''_{Pb}] = 2[V^{\cdot\cdot}_{O}] + [Me^{\cdot}_{Pb}]. \quad (6)$$

Equation (6) reduces to

$$[M'_{Pb}] = 2[V^{\cdot\cdot}_{O}] \quad (7)$$

for a monovalent dopant, which is predominant over the deviation from molecularity, and to

$$[Me^{\cdot}_{Pb}] = 2[V''_{Pb}] \quad (8)$$

for a trivalent dopant under similar conditions.

Further evidence for the occurrence of Eq. (8) is given by Sleight and Linn (*20*), who showed that the concentration of V''_{Pb} in $PbMoO_4$ and $PbWO_4$ can extend to about 14 m/o.

4.2. Ionic Conductivity

4.2.1. $PbMoO_4$

The activation enthalpies for the extrinsic conductivities in $PbMoO_4$ (Fig. 2) are, within the experimental error, the same for all

TABLE II

THE OXYGEN PARTIAL PRESSURE DEPENDENCE OF THE CONCENTRATION OF SEVERAL DEFECTS[a]

Majority defect pair	$\left(\frac{\delta \ln[e']}{\delta \ln P_{O_2}}\right)_{a,T,a_{PbO}}$	$\left(\frac{\delta \ln[V^{\cdot\cdot}_{O}]}{\delta \ln P_{O_2}}\right)_{P,T,a_{PbO}}$	$\left(\frac{\delta \ln[V^{\cdot}_{O}]}{\delta \ln P_{O_2}}\right)_{P,T,a_{PbO}}$
$V^{\cdot\cdot}_{O}, O''_{i}$	$-\frac{1}{4}$	0	$-\frac{1}{4}$
$V^{\cdot\cdot}_{O}, e'$	$-\frac{1}{6}$	$-\frac{1}{6}$	$-\frac{1}{3}$
$V^{\cdot\cdot}_{O}, V''_{Pb}$	$-\frac{1}{4}$	0	$-\frac{1}{4}$
$V^{\cdot}_{O}, e'$	$-\frac{1}{4}$	0	$-\frac{1}{4}$
$e', h^{\cdot}$	0	$+\frac{1}{2}$	$+\frac{1}{2}$

[a] Values for $h^{\cdot}$, V''_{Pb}, and V'_{Pb} can be found by substituting these for e', $V^{\cdot\cdot}_{O}$, and $V^{\cdot}_{O}$, respectively, and changing the sign.

samples. From this we conclude that the same species is responsible for the conductivity. Equations (2), (7), and (8) predict that doping with Na should increase and doping with Bi or Y should decrease the oxygen vacancy concentration. Since the conductivities of sodium-doped crystals are higher and those of bismuth- or yttrium-doped crystals lower than those of the undoped crystals, we assume that $V_O^{\cdot\cdot}$ is the mobile ionic defect in $PbMoO_4$.

$PbMoO_4$:Na exhibits extrinsic conductivity over the temperature region investigated. From the slope in the extrinsic region in Fig. 2 the activation enthalpy of migration for the oxygen vacancy was found to be $\Delta H_m = (0.47 \pm 0.03)$ eV.

Equilibrated, nominally pure $PbMoO_4$ crystals show intrinsic conductivity at higher temperatures and extrinsic conductivity at lower temperatures, independent of the preparation history. At high temperatures $[V_O^{\cdot\cdot}]$ is governed by an internal equilibrium which is likely to be the Frenkel disorder in the oxygen sublattice [Eq. (1)], as has also been found in $CaWO_4$ (*21*). Equation (2) cannot be held responsible for the supply of $V_O^{\cdot\cdot}$, because, as has been mentioned already by van Loo (*2*), a_{PbO} has no influence on the conductivity in the temperature range studied. From the high-temperature slope in Fig. 2 we derived the formation enthalpy for the Frenkel disorder equilibrium, viz., $\Delta H_f = (1.50 \pm 0.03)$ eV.

Bismuth- and yttrium-doped crystals show intrinsic conductivity over the entire temperature region with the same activation enthalpy as in nominally pure crystals. We assume, therefore, that $[V_O^{\cdot\cdot}]$ is still governed by Eq. (1). At high dopant concentrations, as in the case of $PbMoO_4$:Y, the electroneutrality condition reads $[Y_{Pb}^{\cdot}] = 2[V_{Pb}^{''}]$. Because of this high $[V_{Pb}^{''}]$ one might have expected extrinsic conduction via $V_{Pb}^{''}$, or, if Eq. (2) had been established at the temperatures involved, an extrinsic conduction via $V_O^{\cdot\cdot}$. The observed intrinsic conduction via $V_O^{\cdot\cdot}$ leads to the conclusion that the mobility of $V_{Pb}^{''}$ is much lower than that of $V_O^{\cdot\cdot}$. This would also account for the fact that equilibrium via Eq. (2) is not established at temperatures at which the conductivity measurements were performed. Only at very high temperatures, in the region of the melting point, can equilibrium via Eq. (2) be established partially, as can be seen from the fact that no extrinsic $V_O^{\cdot\cdot}$ conductivity is observed at lower temperatures.

The anomalous behavior of nonequilibrated and nitrogen-annealed crystals cannot be explained in the simple model outlined above. The 10 to 100 times higher conductivity of as-grown $PbMoO_4$ can be due to the fact that the anti-Frenkel equilibrium has not been established during the relatively rapid cooling of the crystal. The presence of frozen-in anti-Frenkel defects can also be concluded from experiments on crystals equilibrated in air.

The conductivity of nitrogen-annealed crystals is more complicated. We assume that during annealing in nitrogen $[V_O^{\cdot\cdot}]$ increases via Eq. (4). At low temperatures an enhanced extrinsic conductivity is observed. Above about 740°K equilibrium is established in air, as follows from Fig. 2, which shows that the uptake of oxygen reduces $[V_O^{\cdot\cdot}]$.

On the basis of the chemical analysis of the $PbMoO_4$:Na crystal with the highest conductivity, we can calculate $[V_O^{\cdot\cdot}]$ in as-grown and equilibrated nominally pure $PbMoO_4$. This leads to $1.2 \times 10^{18}/cm^3$ in as-grown and $2.2 \times 10^{16}/cm^3$ in equilibrated crystals.

4.2.2. $PbWO_4$

On the basis of arguments similar to those used in the case of $PbMoO_4$, $V_O^{\cdot\cdot}$ is supposed to be the mobile ionic defect in $PbWO_4$, although the Y-doped crystal behaves anomalously (Fig. 3).

Nominally pure and K-doped crystals of $PbWO_4$ show extrinsic conductivity. The

conductivity measurements (Fig. 3) reveal that $[V_O^{\cdot\cdot}]$ in $PbWO_4$:K does not differ significantly from $[V_O^{\cdot\cdot}]$ in nominally pure crystals. This is not surprising in view of the analysis results (Table I).

$PbWO_4$:Bi crystals show intrinsic conductivity. On the basis of the same arguments as those mentioned above we assume that Frenkel disorder in the oxygen sublattice [Eq. (1)] governs $[V_O^{\cdot\cdot}]$.

From Fig. 3 we found for the activation enthalpy of $V_O^{\cdot\cdot}$ migration $\Delta H_m = 0.40 \pm 0.03$ eV, and for the formation enthalpy of Eq. (1), $\Delta H_f = 1.30 \pm 0.04$ eV.

The conductivity of $PbWO_4$:Y does not fit into this picture. $PbWO_4$:Y shows an extrinsic conductivity about two orders of magnitude higher than that of undoped crystals, with a higher activation enthalpy (Fig. 3). Assuming that $V_O^{\cdot\cdot}$ is still the mobile ionic defect, a possible explanation of this anomalous behavior could be that Y^{3+} is not incorporated on Pb^{2+} sites, but on W^{6+} sites. This would result in the formation of YO_3^{3-} groups, possibly associated with $V_O^{\cdot\cdot}$. The higher activation enthalpy is then due to the dissociation of this associate. If this were the case then the dissociation enthalpy could be calculated to be $\Delta H_d = (0.36 \pm 0.06)$ eV.

4.3. Electronic Conductivity

4.3.1. General

From the data in Table II and the observation that even at high temperatures the ionic conductivity is independent of the oxygen pressure, we conclude that the majority defect pair consists of ionic defects at all temperatures involved, for both $PbMoO_4$ and $PbWO_4$.

The concentration of electrons and holes is determined by the deviation from stoichiometry [Eqs. (3) and (4)]. Table II shows also that in a $\log \sigma_e$ versus $\log P_{O_2}$ plot, a slope of $-\frac{1}{4}$ or $+\frac{1}{4}$ is expected for electron or hole conduction, respectively. Slopes with values higher than $-\frac{1}{4}$ and less than $+\frac{1}{4}$ could indicate conduction by both electrons and holes. No dependence on oxygen pressure is expected if equilibrium via Eqs. (5) and (6) is not established.

4.3.2. $PbWO_4$

It is clear from Fig. 7 that hole conduction dominates in nominally pure $PbWO_4$ and $PbWO_4$:K. Slopes of $+\frac{1}{4}$ were found in the temperature region where oxygen-pressure-dependent electronic conductivity can be measured.

Figure 6 shows two slopes for all samples. At low temperatures an activation enthalpy of about 1.10 eV was found. At high temperatures an activation enthalpy of 0.46 eV was observed for $PbWO_4$ and $PbWO_4$:K, and 0.77 eV for $PbWO_4$:Bi.

The observed change in the slope going from low to high temperatures can have several origins, viz., trapping of holes at low temperatures followed by free-hole conduction, trapping of holes and the establishing of equilibrium via Eq. (3) at higher temperatures, or at low temperatures free-hole conduction and the establishing of equilibrium via Eq. (3) at higher temperatures. In view of the experimental results the third possibility is the most likely.

At low temperatures, where the hole concentration is supposed to be determined by the frozen-in deviation from stoichiometry, the activation enthalpy for conduction is correlated with a temperature-dependent mobility. The relatively high slope of 1.10 eV indicates that a hopping type of conduction is present.

From the difference of the two slopes in the case of $PbWO_4$ and $PbWO_4$:K (Fig. 6), we calculated for the formation enthalpy of Eq. (3): $\Delta H_3 = 1.3$ eV. In this calculation $[V_O^{\cdot\cdot}]$ was taken as being temperature independent, which follows from the ionic conductivity data.

In the case of $PbWO_4$:Bi, $[V_O^{\cdot\cdot}]$ is temperature dependent [Eq. (1)]. From the

difference in the high-temperature slopes of $PbWO_4$ and $PbWO_4$:Bi (Fig. 6), we found for the formation enthalpy of the anti-Frenkel disorder $\Delta H_f = 1.2$ eV, which is in good agreement with the value found from the ionic conductivity data (Fig. 3).

4.3.3. $PbMoO_4$

The conductivity curve of $PbMoO_4$:Na (Fig. 4) is similar to that of $PbWO_4$. We assume, therefore, that the same mechanisms are involved. The $\log \sigma_e$ versus $\log P_{O_2}$ measurements, however, show slopes less than $+\frac{1}{4}$, even at high temperatures (1020°K). This indicates a conduction by both electrons and holes. The decrease of the slope in the $\log \sigma_e$ versus $\log P_{O_2}$ plots at lower temperatures (to 0.05 at 700°K) is possibly due to the fact that equilibrium via Eq. (3) is established very slowly when the oxygen pressure is varied.

Figure 5 shows that in undoped $PbMoO_4$, only at low oxygen pressure and high temperature is a negative slope found, indicating electron conduction. We assume, therefore, that at low and moderate temperatures a conduction by both electrons and holes occurs. Their concentrations are determined by the deviation from stoichiometry. The activation enthalpy for migration, calculated from the low-temperature region in Fig. 4, amounts to 1.32 eV. This suggests trapping and/or a hopping type of conduction. At high temperatures a higher slope of about 1.80 eV is found. An obvious possibility is that equilibrium via Eq. (4) can be established at higher temperatures, giving rise to an extra amount of electrons and consequently a high activation enthalpy.

Van Loo (*2*) also performed measurements on the oxygen partial pressure dependence of the conductivity of $PbMoO_4$. At lower temperatures (about 780°K) he found a small positive slope, indicating hole conduction. At this temperature we did not observe predominant hole conduction. A possible explanation for this feature could be that crystals used by van Loo contained more monovalent impurities, or that the deviation from stoichiometry was larger than that in our crystals. In such crystals the hole concentration will be increased. This idea is supported by the observation that the temperature at which the transference numbers of the ionic and electronic conductivities are equal is much lower for van Loo's crystals than for ours (see Table III).

5. Final Remark

Much has been said in the literature about the yellow coloration of $PbMoO_4$ and $PbWO_4$ crystals. Some authors ascribe the coloration to deviations from stoichiometry or molecularity (*2*, *5*, *7*), others to the presence of impurities (*8*, *22*). All authors assume that the coloration is due to the same centre in both compounds.

Our observation that $PbMoO_4$:Na crystals are intensely colored and $PbWO_4$:K crystals are colorless is, however, in striking contrast

TABLE III

TEMPERATURES AT WHICH THE TRANSFERENCE NUMBERS OF THE IONIC AND ELECTRONIC CONDUCTIVITIES ARE EQUAL[a]

Sample	T (°K) at which $t_e = t_i$	Observed type of conduction
$PbMoO_4$	1035	n and p
$PbMoO_4$[b]	680	p
$PbMoO_4$:Na	660	p
$PbMoO_4$:Bi	1060	n and p
$PbMoO_4$:Y	1050	n and p
$PbWO_4$	620	p
$PbWO_4$[b]	690	—
$PbWO_4$:K	560	p
$PbWO_4$:Bi	660[c]	p

[a] The observed type of electronic conduction at that temperature has also been given.

[b] Values found by van Loo (*2*) from emf measurements.

[c] The lowest temperature at which the ionic conductivity could be determined was 660°K.

to the above assumption. In view of this observation and the differences in the conductivities of undoped $PbWO_4$ and $PbMoO_4$, we suggest that the coloration is not due to the same centre in both compounds. However, more experiments are needed to elucidate the nature of the two different centres.

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