Crystal Growth and Electrical Conduction of $PbMoO_4$ and $PbWO_4$

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The phenomenon of the coloration of Czochralski grown single crystals of $PbMoO_4$ and $PbWO_4$ is discussed. This coloration is supposed to be related to an intrinsic point defect. We propose that during the crystal growth a loss of oxygen occurs, and consequently, oxygen deficient crystals are produced. The existence of electronic charge carriers at high temperatures and ionic majority defects in the oxygen sublattice is confirmed by conductivity measurements. The color center is supposed to be an oxygen vacancy that has trapped one or two electrons. On the basis of this simple model, various aspects of the coloration can be understood.

Introduction

The growth of single crystals of both $PbMoO_4$ and $PbWO_4$ has been reported by several authors (*1–9*), most of them using the Czochralski method. $PbMoO_4$ as well as $PbWO_4$ melts congruently and crystallizes in the scheelite structure. The crystal chemistry of scheelites has been treated in full detail elsewhere (*10*). In the last few years the interest in large optically pure single crystals of $PbMoO_4$ has increased because of its application as an acousto-optic light deflector (*1, 4, 6, 8, 9*).

We have grown single crystals of $PbMoO_4$ (mp 1070°C) and $PbWO_4$ (mp 1123°C) for a study on the luminescence of these two compounds. The optical investigations will be reported in three separate papers.

Experimental

We employed the Czochralski method for the growth of single crystals and used crystal grade $PbMoO_4$ and $PbWO_4$ (α-inorganics) as starting materials. The powder was melted in a platinum crucible (contents: ~30 cm³) by means of rf induction-heating (6 kW generator, Philips, PH 1006–22). Temperature stabilization was achieved through control of the grid current of the transmitting valve using a Pt–Pt/10% Rh thermocouple (immersed in the melt) as a sensor, an automatic compensator (Philips, PR 2210 A/21), and a grid current controller (Philips, PH 1653/00). Pulling rates and rotation rates were adjusted by means of a commercial pulling equipment (Philips PH 1670/10). Seed crystals were grown according to de Vries and Fleischer (*5*) by immersing a platinum wire into the melt. A seed crystal was clamped in a seed holder and nearly colorless cylindrical single-crystalline boules several centimeters long with a diameter of 0.6–1.0 cm were grown using a pulling rate of ~1.0 cm/hr and a rotation rate of ~40 rpm. During the growth some evaporation of the melt took place. When the growth was completed the boule was tapered to a diameter of ~0.3 cm and subsequently the content of the crucible was cooled down slowly (~1°/min). Contact between the crystal and the solidified content of the crucible was maintained to prevent cracking. In addition, a cylindrical after-heater was placed around the boule so that large temperature gradients could be avoided. After cooling down to room temperature the crystal boules were annealed in air at ~850°C for several hours and cooled down at a rate of 12°/hr. Table I lists typical impurity contents of as-grown single crystals of $PbMoO_4$ and

TABLE I

TYPICAL IMPURITY CONTENTS OF
CZOCHRALSKI GROWN SINGLE
CRYSTALS OF $PbWO_4$ AND $PbMoO_4$,
IN ppm BY WEIGHT[a]

Element	$PbWO_4$	$PbMoO_4$
Mg	0.9	1.7
Ca	7.6	13.4
V	≤10	≤10
Cr	≤0.02	≤0.02
Mn	0.04	0.03
Fe	0.8	0.8
Co	≤0.04	≤0.04
Ni	≤0.6	≤0.6
Cu	≤0.03	≤0.03
Mo	45	High
Pt	≤0.8	≤0.8
Tl	≤0.1	≤0.1
Bi	25	55

[a] G. P. M. van den Heuvel of this laboratory is gratefully acknowledged for carrying out the atomic absorption analysis.

$PbWO_4$. The starting materials contained a slight excess of $MoO_3(WO_3)$, which was not noticed in the X-ray diffraction patterns. This excess was observed during a DTA experiment[1] on $PbMoO_4$ and $PbWO_4$ powder. In the case of $PbWO_4$, a thermal effect was recorded at 950°C that roughly corresponds to the position of the solidus (970 ± 5)°C in the $PbWO_4$–WO_3 system (11). In $PbMoO_4$ a thermal effect occurs at 656°C. The solidus of the $PbMoO_4$–MoO_3 system lies at 660°C (12). This excess of MoO_3 (WO_3) is probably due to the fact that during the synthesis of $PbMoO_4$ ($PbWO_4$) by firing of PbO and MoO_3 (WO_3) at high temperatures an equimolar ratio of components is not obtained. During a TGA experiment on a $PbMoO_4$ single crystal in a nitrogen atmosphere (p_{O_2}: 10^{-4}–10^{-5} atm) the oxygen content of the nitrogen flow was recorded by means of a mass spectrometer. No detectable evolution of oxygen was observed.

[1] Thanks are due to Dr. A. H. Verdonk and J. H. W. de Wit of the Analytical Laboratory of the University of Utrecht for performing the DTA and TGA experiments.

Coloration of the Crystals

During single crystal growth we noticed a yellow coloring of the crystals, the coloration being more intense if the contents of the crucible had been molten for a longer time. Annealing of the crystals in air did not influence the intensity of the coloration. This phenomenon has been observed previously by others (3, 6–9). The coloration of the crystals is demonstrated in Fig. 1, which shows optical absorption spectra of colorless and colored crystals of $PbMoO_4$ and of $PbWO_4$ at liquid nitrogen temperature. The coloration was always more intense in $PbMoO_4$ than it was in $PbWO_4$. The measurements were carried out with a Perkin–Elmer Spectrophotometer (model EPS3T). The spectra of Fig. 1 agree with those reported in refs. (3), (8), and (9). Apparently, the absorption band that is responsible for the coloring lies at approximately the same wavelength in $PbMoO_4$ and $PbWO_4$ ($\lambda_{max} \simeq 425$ nm), suggesting that the same type of defect might be present in both compounds. EPR experiments[2] were carried out on colored and colorless single crystals to determine whether or not the center responsible for the coloration is paramagnetic. We did not observe any

[2] Dr. J. Kerssen of this laboratory is gratefully acknowledged for carrying out the EPR experiments.
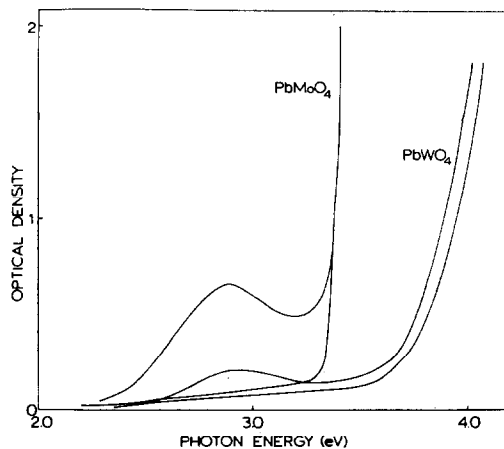

FIG. 1. Optical absorption spectra of colored and colorless single crystals of $PbMoO_4$ and $PbWO_4$ at 77°K.

noticeable difference between colored and colorless crystals. We conclude, therefore, that the color center is not paramagnetic or that the center concentration is too low to be detected with our EPR-equipment [maximum sensitivity: 10^{12} spins/Gauss (13)].

Esashi and Namikata (8) have tentatively ascribed this coloration to impurities and/or nonstoichiometry. They observed an enhanced coloration when the purity of the starting material was lower and when the amount of MoO$_3$ increased. Loiacono et al. (9) arrive at the following conclusions after a thorough investigation of the various aspects of the growth of PbMoO$_4$ single crystals. First, the addition of an excess of either MoO$_3$ or PbO to the melt did not have any effect on the degree of coloration. Second, annealing of colored PbMoO$_4$ crystals in oxygen at elevated temperatures resulted in a decrease of the intensity of the yellow coloration, as has also been reported by Azarbayejani (7). Third, no correlation has been observed between the impurity content and the final boule color. Bonner and Zydzik (6) have reported that the material evaporated from the PbMoO$_4$ melt contains approximately equal amounts of PbO and MoO$_3$. Making use of this observation, Loiacono et al. (9) concluded that the coloration is probably not due to a deviation from stoichiometry. They have tentatively assumed that impurities are responsible for the coloring but a specific impurity has not been identified.

Since their conclusions concerning the nature of the additional absorption in PbMoO$_4$ are rather vague, we have tried to correlate the coloration with an intrinsic defect, the concentration of which depends on the degree of nonstoichiometry. This was done by measuring the transference numbers of the ionic and electronic conductivity in addition to the total electrical conductivity as a function of temperature and of the partial pressure of oxygen.

Conductivity Measurements

As Schmalzried (14) has pointed out, two independent thermodynamic variables must be taken into account in addition to

pressure and temperature in the case of ternary compounds, e.g., the thermodynamic activities of two components such as p_{O_2} and a_{PbO} or p_{O_2} and a_{MoO_3} for PbMoO$_4$. During the measurements of the total electrical conductivity of PbMoO$_4$ some MoO$_3$ (or PbO) powder was placed in a platinum crucible near the crystal and the partial pressure of oxygen was fixed. However, no substantial influence of this addition was noticeable, except for the fact that reproducible results were obtained in the temperature region 500–1000°K. Furthermore, no systematic difference between the conductivities of colorless and colored crystals was observed.

Since electronic as well as ionic conduction is expected in these compounds we measured the transference numbers of the electronic and ionic species in the temperature region 550–1250°K ($t_{ion} = \sigma_i/(\sigma_i + \sigma_e)$; $t_{el} = \sigma_e/(\sigma_i + \sigma_e)$). To do this we measured the EMF of an electrochemical cell composed of a single-crystalline disk of PbMoO$_4$ (PbWO$_4$) with different oxygen partial pressures on each side of the disk. This method has been described well in the literature (15–18). If ionic conduction predominates an EMF is built up, which is represented by:

$$E_i = \frac{RT}{4F} \ln(p_{O_2}^I/p_{O_2}^{II}) \qquad (1)$$

If electrons or electron holes are the dominant charge carriers, the cell will be short-circuited and hence the EMF will be zero. If the value of the EMF lies between E_i and zero the transference numbers of the ionic and the electronic species can be deduced from:

$$t_i = \frac{E_{exp}}{E_i}; \qquad t_e = 1 - t_i \qquad (2)$$

The construction of the EMF-cell is shown schematically in Fig. 2. The EMF was measured with an electrometer (Keithley, type 610BR). Below 550°K no reliable measurements could be made. In a preliminary experiment using the guard-ring technique (16) we noticed that surface conduction was negligible. We used pure oxygen ($p_{O_2} = 1$ atm) and air ($p_{O_2} = 0.2$ atm) flows to fix $p_{O_2}^I$ and $p_{O_2}^{II}$. At each temperature the two flows were
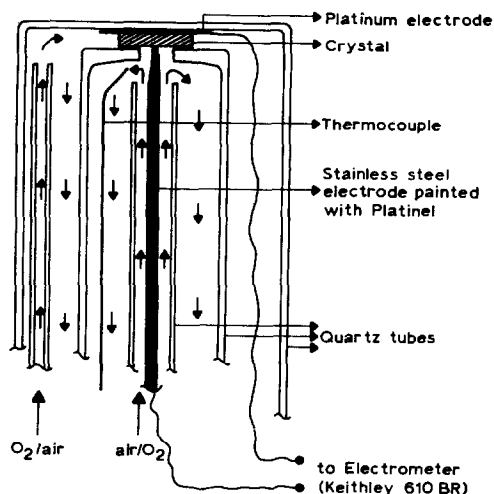
FIG. 2. Schematic representation of the EMF cell used for the determination of transference numbers. Separation of the two gas flows was achieved by pressing the polished flat end of the middle quartz tube onto the crystal, which was painted with platinel.

FIG. 4. Transference numbers for the ionic (t_i) and the electronic (t_e) species in $PbWO_4$.

interchanged to eliminate the contribution of offset voltages, which are presumably due to thermoelectric voltages in the wiring of the cell. In this way the EMF could be determined reproducibly. Typical results are shown in Fig. 3 for $PbMoO_4$ and in Fig. 4 for $PbWO_4$.
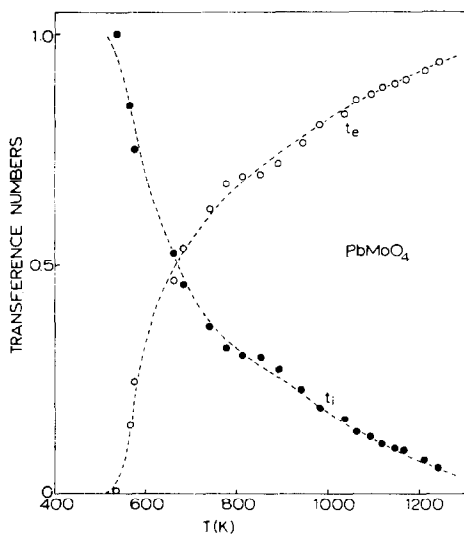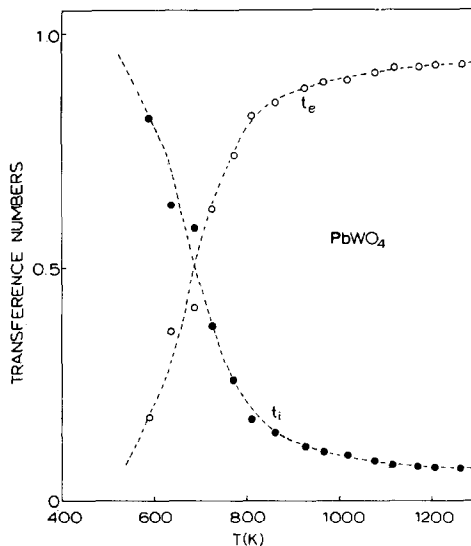

FIG. 3. Transference numbers for the ionic (t_i) and the electronic (t_e) species in $PbMoO_4$.

It is obvious that at low temperatures the conduction is predominantly ionic, whereas at higher temperatures the contribution of the electronic conduction increases. Kumar et al. (18) have observed the same phenomenon in ZrO_2. A similar behavior has been reported by Mitoff (16) for MgO single crystals.

The total electrical conductivity was measured at 1 kHz with an ac impedance bridge (General Radio, type 1608A) with an external oscillator (G.R. type 1210C) and an amplifier-null detector (G.R. type 1232A). At temperatures above 1000°K the conductivity could not be measured reliably, probably owing to irreversible processes that affect the crystal, resulting in a deviation from the stoichiometric composition.

Despite the tetragonal symmetry of scheelites, no anisotropic conduction was observed in $PbMoO_4$ single crystals. $CaWO_4$, investigated by Rigdon and Grace (19) also fails to show any anisotropy of the electrical conductivity. Their explanation, based on the quasi fourfold symmetry of scheelites (20) is also valid for $PbMoO_4$.

The total ac conductivity of a $PbMoO_4$ single crystal was measured as a function of the partial pressure of oxygen (range 5–760

mm Hg) at fixed temperatures. These experiments were carried out up to 1000°K in a nickel conductivity cell, which could be evacuated. In this cell the oxygen partial pressure could be fixed, whereas the total pressure in the system was always kept at 1 atm. The results of these experiments at different temperatures are gathered in Fig. 5. At temperatures below ~550°K the conductivity does not depend on the partial pressure of oxygen, indicating that ionic conduction predominates in that temperature region. This conclusion agrees with the fact that at $T < 550$°K the transference number for the ionic species tends to approach unity. At higher temperatures the conductivity starts to become p_{O_2}-dependent owing to an increasing electronic conductivity. The measurements at 774°K show a positive slope in the $\log \sigma$ versus

$\log p_{O_2}$ plot (Fig. 5) corresponding to hole conduction in this pressure region. At higher temperatures a minimum in the $\log \sigma$ versus $\log p_{O_2}$ plot appears indicating a gradual change from p-type to n-type electronic conduction in this pressure range. At 1005°K the slope being negative has a value of -0.25. Similar behavior is met with in ZrO_2 (18) and Al_2O_3 (21). In a preliminary study of the thermoelectric power of $PbMoO_4$ (in air) p-type electronic conduction was observed at temperatures below 900°K. Unfortunately measurements at higher temperatures were not possible with our equipment so that the transition from p to n-type electronic conduction could not be confirmed by the thermoelectric power experiment. Although the pressure range in which we studied the conductivity behavior of $PbMoO_4$ is limited, we will discuss the majority defects in $PbMoO_4$ and try to correlate those defects with the coloration.

Discussion

Schmalzried (14) has given a general treatment of possible disorder types (ionic and electronic) in stoichiometric and non-stoichiometric AB_2O_4 compounds (spinels). His outline has been applied to scheelites $(CaWO_4)$ by Rigdon and Grace (19). They neglect highly charged defects and conclude that oxygen vacancies and oxygen interstitials are the predominant ionic defects and that the electronic charge carriers are minority defects in the temperature range: 900–1300°C. The oxygen annealing experiments on colored crystals (7, 9) indicate that oxygen is a rather mobile species in $PbMoO_4$. In addition, Nassau and Loiacono (22) have concluded from reduction experiments with $CaWO_4$, that oxygen is very mobile at relatively high temperatures. Therefore, we assume that in $PbMoO_4$ and $PbWO_4$ the migration of defects in the oxide sublattice contributes significantly to the conductivity. The question whether the migration of lead ions makes an essential contribution to the conductivity can only be answered by diffusion experiments. Further, the electronic defects are minority defects (cf. Figs. 3 and 4).
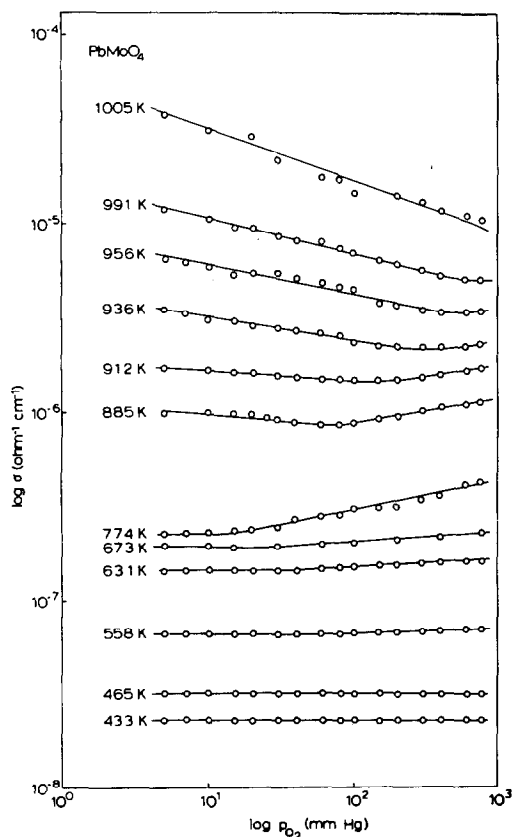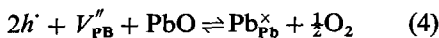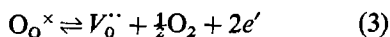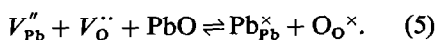

FIG. 5. Electrical conductivity of PbMoO₄ as a function of p_{O_2} at different temperatures.

Since the crystals of $PbMoO_4$ and $PbWO_4$ will always contain a slight excess of MoO_3 (WO_3) the predominant ion defects will be $V_O^{\cdot\cdot}$ and V_{Pb}''. Exchange of oxide ions in the crystal with oxygen in the surrounding atmosphere can be written as:

$$O_O^\times \rightleftharpoons V_O^{\cdot\cdot} + \tfrac{1}{2}O_2 + 2e' \qquad (3)$$

$$2h^\cdot + V_{PB}'' + PbO \rightleftharpoons Pb_{Pb}^\times + \tfrac{1}{2}O_2 \qquad (4)$$

Combining Eqs. (3) and (4) yields:

$$V_{Pb}'' + V_O^{\cdot\cdot} + PbO \rightleftharpoons Pb_{Pb}^\times + O_O^\times. \qquad (5)$$

Thus, it is clear that at low oxygen pressures the electronic conduction will be n-type, whereas at high oxygen pressures the electronic conduction will be p-type. This has indeed been observed (cf. Fig. 5). Consequently, the dependences of n and p on p_{O_2} read:

$$\left(\frac{\partial \ln n}{\partial \ln p_{O_2}}\right)_{a_{PbO}} = -\frac{1}{4} \qquad (6)$$

$$\left(\frac{\partial \ln p}{\partial \ln p_{O_2}}\right)_{a_{PbO}} = +\frac{1}{4} \qquad (7)$$

Only at 1005°K a negative slope of -0.25 is observed. The smaller slope values at lower temperatures presumably arise from the fact that the transition from p to n-type electronic conduction is not sharp but extends over a rather wide pressure range. The fact that this transition is observed in the pressure range studied is not obvious. It depends on various parameters, e.g., the temperature variations of the mobilities of the electrons and the electron holes, and on their concentrations, which vary with temperature, oxygen partial pressure, and the degree of nonstoichiometry. Unfortunately these relations are unknown. Despite these limitations we propose a process that may lead to the creation of color centers during the single crystal growth of $PbMoO_4$ and $PbWO_4$.

When $PbMoO_4$ ($PbWO_4$) crystals are grown, some loss of oxygen occurs. Thus an oxygen deficient single crystal is pulled from the melt. We assume that oxygen vacancies are the predominant ionic defects in colored crystals. This assumption is not contradicted by the conductivity results. At room temperature or below, oxygen vacancies will probably trap one or two electrons. The color centers so formed may be responsible for the additional absorption band in colored crystals (cf. Fig. 1.). If the majority of the vacancies has trapped two paired electrons, it is explained why no EPR signal has been observed. In addition the resemblance of the extra absorption bands in colored $PbMoO_4$ and $PbWO_4$ is not unexpected in view of this model. However, this model implies that this type of coloration should not be restricted to $PbMoO_4$ and $PbWO_4$. As a matter of fact a coloration of Czochralski-grown $CaMoO_4$ crystals has been reported by Vishnevsky et al. (23). Recently, Becker and Scharmann (24) have reported an additional absorption in $CaWO_4$ single crystals at photon energies below the absorption edge. A green emission has been observed upon excitation in this extra absorption band at 4.2°K. Becker and Scharmann have ascribed this phenomenon to a center, consisting of a WO_3 group replacing a WO_4^{2-} group, which is identical with a neutral oxygen vacancy ($V_O^\times$). Koehler and Kikuchi (25) have reported the presence of $(WO_3)^\times$ centers in $CaWO_4$, grown from a melt containing a slight excess of WO_3 (1 %). These crystals, too, were weakly colored. The observation of the more intense coloration in $PbMoO_4$ with respect to $PbWO_4$ can be explained by the fact that oxygen loss occurs more easily in $PbMoO_4$ since in general molybdates are less stable compounds than tungstates (10).

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