# Determination of the potassium composition in $K_xMoO_3$ ($x$ = 0.1–0.5) by EDX spectroscopy

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It is known that the 'blue bronze' $K_{0.3}MoO_3$ is a one dimensional conductor along the crystallographic $b$-axis and the metal-semiconductor transition of a Pierls type occurs at about 180 K [1, 2], whereas the 'red bronze' $K_{0.33}MoO_3$ is highly anisotropic semiconductor at all temperatures [3, 4].

In general, transition metal oxides $M_x$—$T_aO_b$ exhibit various structures and a variety of physical properties, depending on various amounts of $x$ a third element M, where M is usually an alkali metal or an alkali earth metal, which donates its electron(s) to the conduction band of the host metal. With regard to $K_xMoO_3$ belonging to a class of ternary transition metal oxides, structural determinations and/or measurements of physical properties are mostly limited to $x = 0.3$ or $x = 0.33$ [5–7].

Recently, Hirata *et al.* [8] tried to prepare $K_xMoO_3$ with $x = 0.1$ to 0.5 by a solid state reaction, and infrared reflectivity spectra of the reaction products were measured in the region with wavenumbers from 400 to 4000 $cm^{-1}$ at room temperature. In this situation, it became a matter of importance to know the potassium composition of the predominant phase(s) in $K_xMoO_3$ whose structure and lattice parameters are determined and which is responsible for three phonon peaks.

Knowledge about the concentration of potassium in a phase tells if phase separation would occur in a solid state reaction and/or whether the molybdenum bronzes with K composition, different from the 'blue bronze' $K_{0.3}MoO_3$ or the 'red bronze' $K_{0.33}MoO_3$, are formed. The objective of the present work is to determine the potassium composition of the predominant phase(s) in $K_xMoO_3$ prepared by the solid state reaction:

$$\frac{x}{2}MoO_3 + (1 - x)MoO_2 + \frac{x}{2}K_2MoO_4 \rightarrow K_xMoO_3$$

$$(x = 0.1 \text{ to } 0.5).$$

Carefully ground and mixed reactants were pressed at 50 MPa into pellets; these pellets were subjected to CIP (Cold Isostatic Pressing) at 200 MPa, vacuum-sealed into quartz tubes at a pressure $10^{-5}$ Torr, and sintered at 435° C for 96 h. *In situ* diffuse reflectance Fourier transform infrared spectroscopy confirmed that no decomposition or volatalization of any reactants occurs under our sample preparation conditions. X-ray diffractometry revealed that all reaction products are not of single phase; $K_xMoO_3$ with $x = 0.1$ to 0.2 contains some quantity of $MoO_3$ which is somewhat expanded due to intercalation of K-ions, $K_xMoO_3$ with $x = 0.3$ is almost of single phase, and $K_xMoO_3$ with $x = 0.33/0.4$ and $x = 0.5$ contain traces of the 'blue bronze' and the 'red bronze', respectively. An EDAX PV 9100 spectrometer was applied to determine the potassium composition of the predominant phase(s) in $K_xMoO_3$ with $x = 0.1$ to 0.5, based on MoL$\alpha$ (2.29 KeV) and KK$\alpha$ (3.31 KeV) using $K_2MoO_4$ for reference. No elements other than molybdenum and potassium were present except for oxygen in the reaction products which was not analyzed in the present work. In $K_xMoO_3$ with $x = 0.1$, 0.2 and 0.3, plate-like particles with a blue colour are formed, whereas platelets with a red colour are formed with $x = 0.3$ and $x = 0.4$, as represented in Fig. 1 for $K_xMoO_3$ having $x = 0.3$ and $x = 0.33$. With $x = 0.5$, granular particles with a light blue colour are observed, indicating the formation of a different phase from that in $K_xMoO_3$ with $x = 0.1$ to 0.4.

Table I shows the potassium composition determined from an area of 1000 × 800 $\mu m^2$ or 100 × 80 $\mu m^2$ of the reaction products (area analysis) and such particles themselves as shown in Fig. 1 (point analysis). The potassium composition determined from a wide area of the reaction products, $x_{exp}$(I), is close to the nominal one, $x$, in $K_xMoO_3$, whereas the potassium composition from a small area of the reaction products, $x_{exp}$(II), is equal to or larger than $x_{exp}$(I). The composition (II) varied somewhat from place to place (chosen at random for analysis). Nevertheless, it is of particular interest to note $x_{exp}$ (II) $\simeq$ 0.3, in spite of $x_{exp}$(I) $\simeq x$ in $K_xMoO_3$ with $x = 0.1$ and $x = 0.2$. This reflects that the formation of the 'blue bronze'

TABLE I The potassium composition in $K_xMoO_3$ ($x$ = 0.1 to 0.5) determined by EDX spectroscopy.

| $x$ (nominal) | $x_{exp}$(I)* | $x_{exp}$(II)† | $x_{exp}$(III)‡ |
|---|---|---|---|
| 0.1 | 0.11 | 0.26 | 0.28 |
| 0.2 | 0.20 | 0.28 | 0.32 |
| 0.3 | 0.31 | 0.32 | 0.33 |
| 0.33 | 0.35 | 0.35 | 0.34 |
| 0.4 | 0.41 | 0.42 | 0.39 |
| 0.5 | 0.57 | 0.58 | > 0.45 |

*From an area of 1000 × 800 $\mu m^2$.
†From an area of 100 × 80 $\mu m^2$.
‡Average of three particles or more in point analysis.

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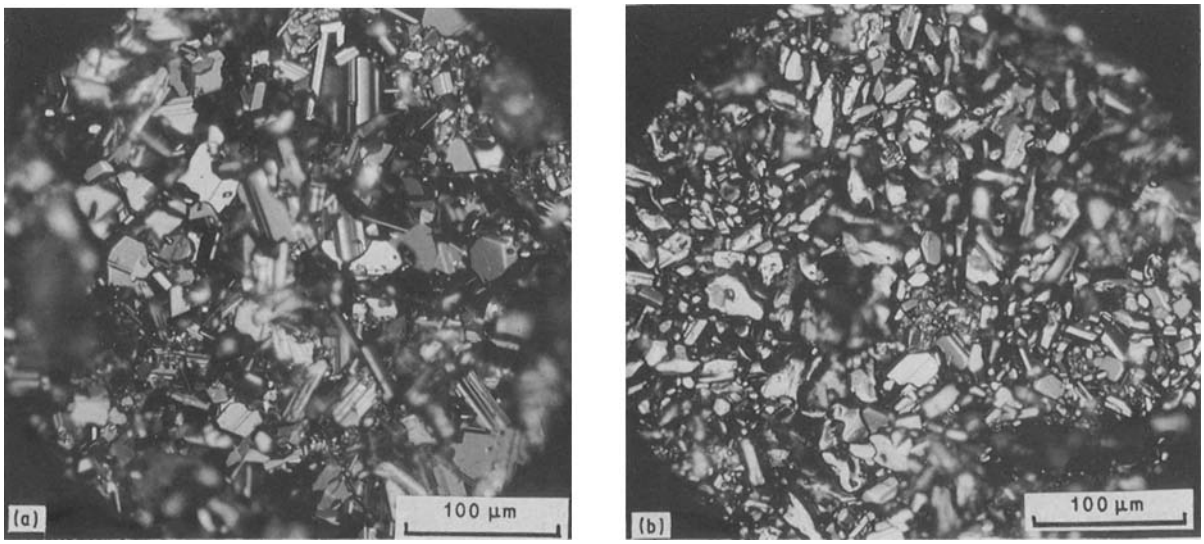


*Figure 1* Comparison of microstructure and colour of the reaction products $K_xMoO_3$ with the nominal potassium composition: (a) $x = 0.3$ and (b) $x = 0.33$.

$K_{0.3}MoO_3$ is preferred in combination with another phase of a lower potassium composition, i.e. phase separation occurs, during the solid state reaction to yield $K_xMoO_3$ with $x = 0.1$ and 0.2.

In fact, X-ray diffractometry on $K_xMoO_3$ with $x = 0.1$ and 0.2, demonstrates a few reflection peaks due to $MoO_3$ that is somewhat expanded by intercalation of K-ions plus reflection ascribed to 'blue bronze'. Also, infrared reflectivity spectra of $K_xMoO_3$ with $x = 0.1$ and 0.2 [8], reveals traces of the Mo–O–Mo bridging band at 820 $cm^{-1}$ and the Mo = O terminal band at 999 $cm^{-1}$ for $MoO_3$ [9], in addition to three phonon peaks due to the predominant phase. In $K_xMoO_3$ with $x = 0.33$ and $x = 0.4$, the 'red bronze' is predominantly formed. With $x = 0.5$ the predominant phase has a tetragonal structure and its lattice parameters are comparable to that given in [10], while the predominant phases in $K_xMoO_3$ with $x = 0.1$ to 0.4 are all monoclinic [5, 6, 11]; it is not well understood why $x_{exp}(II) > x$ for $x = 0.4$ and $x = 0.5$, however, it seems that appearance of the phase with a different structure causes a higher $x_{exp}(II)$ than $x$ in $K_xMoO_3$ with $x = 0.5$.

Fig. 2 shows a scanning electron micrograph for the reaction products as represented for $K_xMoO_3$ with $x = 0.2$. Though no attempt has been made to subject all particles as shown in Fig. 2 to EDX, $x_{exp}(III)$'s represents the average of at least three particles in point analysis within an area of 100 × 80 $\mu m^2$ of the reaction products. It is worthwhile noting that $x_{exp}(II) \simeq x_{exp}(III)$ in $K_xMoO_3$ with $x = 0.1$ to 0.4. It should also be noticed that $x_{exp}(II)$'s or $x_{exp}(III)$'s tend to increase by 5% or so with $x$ in $K_xMoO_3$. This suggests a possibility that the molybdenum bronzes with K-composition slightly different from the 'blue bronze' and/or the 'red bronze' are formed by solid state reactions.

In fact, the lattice parameter 'a' and/or 'c' for the predominant phase (monoclinic) in $K_xMoO_3$ with $x = 0.1$ to 0.4 showed a slight tendency to increase with $x_{exp}(II)$, and the three phonon peaks in the infrared reflectivity spectra also shift upwards with $x_{exp}$ (II); $x_{exp}(II)$ or $x_{exp}(III)$ is considered to represent the potassium composition for the predominant phase in the reaction products.

Thus, the determination of the potassium composition in $KMoO_3$ (for $x = 0.1$ to 0.5) concludes that solid state reactions have a potential for preparing the molybdenum bronzes with different potassium composition from the 'blue bronze' $K_{0.3}MoO_3$ and/or the 'red bronze' $K_{0.33}MoO_3$. It is of interest to measure physical properties of the molybdenum bronzes with variable amount of potassium, in spite of the two-phase nature of the reaction products.

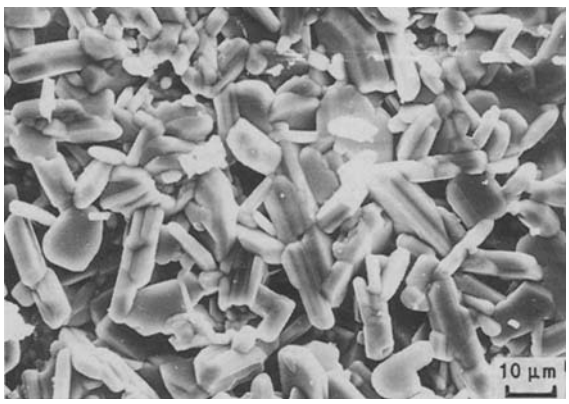


*Figure 2* Scanning electron micrograph for the reaction product $K_xMoO_3$ with $x = 0.2$; magnification × 1000.

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