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# LOW TEMPERATURE SYNTHESIS OF POTASSIUM DOPED BARIUM LEAD PEROVSKITES $K_xBa_{1-x}PbO_{3-y}$ FROM HYDROXIDE MELTS

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ABSTRACT

Perovskite type barium oxoplumbates can be grown at low temperatures via chemical synthesis from alkali hydroxide melts. Strongly oxidizing conditions and low K/Ba ratio lead to the formation of the ternary phase $BaPbO_3$ whereas less oxidizing conditions and high K/Ba ratio favour the formation of the quaternary solid solution $K_xBa_{1-x}PbO_{3-y}$ with tetragonal symmetry. Mixed valence PbII/PbIV quaternary phases can similarly be prepared by anodic deposition from hydroxide melts in closed systems; partial substitution by rare earth ions is possible. Ternary and quaternary oxoplumbates can be reduced electrochemically in aqueous electrolytes at ambient temperature under formation of lead metal.

MATERIALS INDEX: Perovskites, lead oxides, molten salts

## Introduction

The low temperature preparation of solids via hydroxide melts has found increasing application recently as a useful technique for synthesis and crystal growth of oxometallates with metal ions in high oxidation states. Via chemical reactions in alkali hydroxide melts $Cu^{3+}$ and $Bi^{5+}$ compounds can be obtained e.g. $NaCuO_2$ (1), $La_{2-x}A_xCuO_4$ (A = Na, K, Rb, Cs) (2), $LiSr_3BiO_6$, $Li_6RbBiO_6$ (3) and superconducting phases $K_xBa_{1-x}BiO_3$ (4). Electrochemical anodic deposition from hydroxide melts similarly yield frequently single crystalline materials e. g. $KBiO_3$ (5), $K_xBa_{1-x}BiO_3$ (6) or substituted polynary oxobismutates $K_xBa_{1-x}M_yBi_{1-y}BiO_3$ (M = Ln, Sn, Cd, Pb) (7).

We have performed investigations on the low temperature synthesis of single crystals of the distorted perovskite $BaPbO_3$. Although the lead ions have $d^{10}$ closed shell electronic configuration the compound exhibits semimetal properties which have been explained by an overlap of the oxygen 2p band with the lead 6s band (8). Here we report on the preparation of the ternary lead phase and of new potassium substituted quaternary compounds via chemical and electrochemical preparation from potassium hydroxide melts.

## Experimental

Chemical synthesis of barium oxoplumbates has been performed via two different procedures with analytical grade starting materials. At 400°C crystals were grown in alumina crucibles in ambient atmosphere from mixtures consisting of PbO or Pb (5 g), $BaO_2$ (5 g) and KOH (9 g). At 250°C the reaction was carried out in closed Teflon containers with mixtures of PbO (1.5 g) and $PbO_2$ (1.5 g), $Ba(OH)_2(H_2O)_8$ (3 g) and KOH (45 g).

Electrochemical deposition was achieved by following a procedure described previously (7). Sealed Teflon containers were equiped with platinum wires as electrodes (0.3 mm diameter). The reaction mixture consisted of KOH (45 g), PbO (3 g) and $Ba(OH)_2(H_2O)_8$ (3 g). The process was carried out isothermally at 250°C and with a constant voltage of 0.9 V. After reaction times between 6 h and 24 h the reaction vessel was opened and the electrode withdrawn from the melt. The deposited material was cooled to room temperature, removed from the anode and washed free of adhering melt matrix by treatment with dilute mineral acid.

For comparison purposes polycrystalline $BaPbO_3$ was prepared from stoichiometric mixtures of $BaCO_3$ and PbO by repeated calcination and intermediate grinding with stepwise increased temperatures between 600°C and 950°C under oxygen atmosphere. After a final sintering step at 950°C the samples were either slowly cooled down to room temperature or quenched in liquid nitrogen.

X-ray powder patterns were recorded by the Guinier technique and by powder diffractometer measurements (Siemens D 5000, primary beam monochrometer, position sensitive detector system). A Hitachi S-520 scanning electron microscope equiped with a Kevecs analytical system served for the determination of the metal stoichiometry; single crystals were scanned across a fresh crystal surface obtained by polishing in order to detect inhomogeneities of the bulk material. Resistivity and magnetic measurements were performed with a modified AC susceptometer (Lake Shore Model 7000) and a Faraday balance down to 12 K. Electrochemical studies at 300 K were carried out in aqueous electrolytes with three electrode cells and working electrodes consisting of single crystals mixed with 1 % wt Teflon powder and ground pressed into platinum grids. The potential of the working electrodes was measured with a standard calomel electrode as reference system. Iodometric titration has been used to evaluate the formal average oxidation states of the products.

## Results and Discussion

The reaction of PbO or Pb with barium peroxide in potassium hydroxide melt at 400°C in ambient air was found to result in the formation of single crystals of $BaPbO_3$. The black crystals exhibit cubic morphology with crystal edge dimensions up to 0.5 mm. Powder patterns of the material could be indexed with an orthorhombic unit cell (table 1); the values observed correspond well with those published in the literature (9). Analytical measurements (EDX) showed that no potassium ions from the melt had been incorporated into the material under these conditions. Resistivity measurements confirmed the metallic character in terms of the temperature coefficient of the electronic conductivity as observed earlier (9).

Reactions performed at a reduced temperature of 250°C in closed Teflon vessels lead to the formation of black crystals with cubic morphology with a maximum edge size of 0.5 mm. Preliminary EDX measurements revealed a significant potassium content. Further detailed examination of these crystals with respect to chemical composition were performed after abrasing and polishing in order to exclude surface effects with at least five measurements on each crystal at different spots. These measurements confirmed the bulk nature of potassium incorporation and simultaneously revealed inhomogeneities of the crystal composition. In table 2 data are listed for five different crystals of one batch of the minimum and maximum potassium content observed. The stoichiometry varies between $K_{0.10}Ba_{0.89}PbO_{3-y}$ and $K_{0.26}Ba_{0.77}PbO_{3-y}$ with an estimated experimental error of +/- 0.02 for the metal ratio. Inhomogeneities in the K content and distribution are found both within individual crystals and between different crystals. The results demonstrate the existence of a solid solution $K_xBa_{1-x}PbO_{3-y}$ (~ 0.1 < x < ~ 0.26). The averaged stoichiometry corresponds to $K_{0.17}Ba_{0.82}PbO_{3-y}$. From iodometric titrations a nominal average oxidation state for Pb of + 3.67 was calculated which would correspond formally to an oxygen deficiency of y = 0.24.

TABLE 1

Lattice Parameters of Ternary and Quaternary Oxoplumbates

| Compound | Synthesis conditions | Lattice parameters |
|---|---|---|
| $BaPbO_{2.93}$ | sintering,<br>quenched from 950 °C | a=602.1 pm, b=603.1 pm,<br>c=859.7 pm; o.rh. |
| $BaPbO_3$ | KOH, 400 °C<br>open crucible | a=602.6 pm, b=606.2 pm,<br>c=850.6 pm; o.rh. |
| $K_{0.1}Ba_{0.82}PbO_{2.76}$ | KOH, 250 °C<br>closed system | a=601.5 pm<br>c=860.4 pm; tetr. |
| $K_xBa_{1-x}PbO_{3-y}$ | KOH, 250 °C<br>anodic deposition | a=601.3 pm,<br>c=860.9 pm; tetr. |
| $K_xBa_{1-x}Tb_yPb_{1-y}O_{3-y}$ | KOH, 250 °C<br>anodic deposition | a=426.6 pm; cubic |

Powder diffraction patterns revealed that the quaternary compounds do not exhibit orthorhombic symmetry like the ternary phases $BaPbO_3$. The X-ray data could be indexed with a tetragonal unit cell (table 1); as a consequence of the compositional inhomogeneity range the Bragg reflections were found to be rather broad. The relation of the tetragonal unit cell with the simple perovskite cell $a_p$ is $a \sim a_p \cdot 2^{1/2}$ and $c \sim 2\ a_p$. The partial isomorphous substitution of barium ions by potassium ions results thus in the disappearance of orthorhombic symmetry, an elongation of the c axis of ~ 10 pm and an increase in unit cell volume of ~ 0.3 %.

Similar structural changes were observed for the transition from $BaPbO_3$ to oxygen deficient $BaPbO_{3-y}$. The latter was obtained by quenching sintered polycrystalline $BaPbO_3$ from 950°C (1 bar $O_2$) with liquid nitrogen. As determined by iodometric titration the product stoichiometry corresponds to $BaPbO_{2.93}$ equivalent to a mean oxidation state of + 3.86 for Pb. This phase exhibits an orthorhombic unit cell (table 1); as compared to stoichiometric $BaPbO_3$ obtained by slow cooling of the latter from 950°C (1 bar $O_2$) the orthorhombicity is clearly reduced; the elongation of the c axis amounts to 9 pm as found above for the transition from $BaPbO_3$ to $K_xBa_{1-x}PbO_{3-y}$. We conclude therefore that the structural changes (related to the tilting mode of the $PbO_6$ octahedra) in the latter case are likely to be dominated by the reduced nature of the system rather than by the isomorphous substitution on the perovskite A sites.

TABLE 2

Cation stoichiometry as determined by EDX for five crystals $K_xBa_{1-y}PbO_3$ from one batch (crystals cleaved and polished); indicated are local minimum and maximum stoichiometry values K for individual crystals

| | $K_{min}$ | $K_{max}$ |
|---|---|---|
| 1 | $K_{0.18}Ba_{0.81}Pb_{1.0}$ | $K_{0.22}Ba_{0.78}Pb_{1.0}$ |
| 2 | $K_{0.10}Ba_{0.89}Pb_{1.0}$ | $K_{0.20}Ba_{0.78}Pb_{1.0}$ |
| 3 | $K_{0.10}Ba_{0.87}Pb_{1.0}$ | $K_{0.14}Ba_{0.80}Pb_{1.0}$ |
| 4 | $K_{0.13}Ba_{0.84}Pb_{1.0}$ | $K_{0.14}Ba_{0.84}Pb_{1.0}$ |
| 5 | $K_{0.13}Ba_{0.85}Pb_{1.0}$ | $K_{0.26}Ba_{0.77}Pb_{1.0}$ |

The interpretation of the reduced state of the quaternary potassium phase can be based on two models. The most simple explanation is based on a balance of charges via defects in the oxygen sublattice, which is a well-known phenomenon in perovskite chemistry; defect concentrations up to $y = 0.5$ in $ABO_{3-y}$ phases have in fact been described (10). It has to be considered here, however, that the synthesis of the potassium compound proceeds in a hydroxide flux which provides a possible alternative mode for (total or partial) charge compensation by hydroxyl groups on anion lattice sites. The two extreme cases in terms of composition are thus

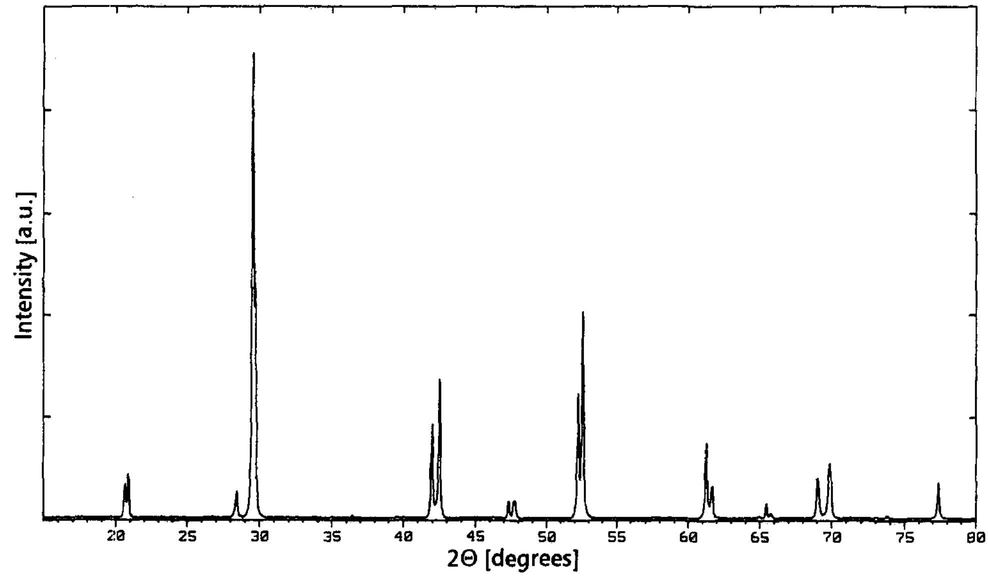
$$K_{1-x}Ba_xPbO_{3-y} \quad \text{and} \quad K_{1-x}Ba_xPbO_{3-z}(OH)_z$$

where y and z are determined both by the extent of isomorphous substitution and by the mean oxidation state of the lead ions.

The formation of the K subsituted quaternary phases from hydroxide melts is clearly dependent upon the reaction conditions. Potassium substitution is observed at lower temperatures in closed systems with a drastically increased K/Ba ratio in the melt. The use of closed systems leads to the preservation of the water content (as present in commercial KOH) in the melt. At higher temperatures in open systems the $H_2O$ concentration is rapidly lowered. Furthermore the use of closed systems decreases the amount of oxygen uptake by the melt. Both effects and the absence of additional peroxide cause a decrease of the oxidation potential of the hydroxide melt in closed systems and favour the formation of lower oxidation states. The increase of the K/Ba ratio by more than a factor of 10 in the melt is expected to favour the incorporation of potassium in the barium oxoplumbate. The inhomogeneity of the products is a general problem of the synthesis technique in the case of materials with an extended solid solution range. To avoid this phenomenon a rather rigid control of experimental parameters such as water activity, oxygen partial pressure over the melt, temperature and concentration gradients in the melt is required.

FIG. 1

X-ray powder diagram of $K_xBa_{1-x}PbO_{3-y}$ obtained by electrochemical preparation.



The *electrochemical* synthesis from $KOH/Ba(OH)_2/PbO$ at 250°C in closed cells at constant potential leads to the growth of black intergrown cubic crystals on the platinum anode. X-ray powder diffraction data from material prepared by anodic oxidation demonstrate that it is isostructural with $K_{0.17}Ba_{0.82}PbO_{3-y}$ obtained by chemical synthesis as described above. Fig. 1 displays the characteristic diffractogram; tetragonal lattice parameters are given in table 1. Analytical data from atomic absorption spectroscopy yield an averaged potassium content of the phase corresponding to $x = 0.20$. The mean oxidation state of lead was found to be + 3.86 by iodometric titration. In terms of materials yield (at equal reaction times) the electrochemical procedure turned out to be superior to the chemical process. Control experiments showed that no anodic product is formed when PbO is replaced by $PbO_2$.

In fig. 2 the resistivity curve for a single crystal of the potassium phase prepared by electrochemical synthesis is given for the temperature range 15 - 200 K. From the negative temperature coefficient of the electronic conductivity we conclude that the material has metallic properties. Magnetic measurements were performed with a Faraday balance. We observed temperature independent diamagnetism between 80 K and 320 K; calculation of the mass susceptibility yielded a value of $\chi = - 3.8 \cdot 10^{-6}\ cm^3g^{-1}$. The expected Pauli paramagnetism is obviously rather weak, the susceptibility is dominated by the diamagnetic moments of the electron rich elements.

For the corresponding Bi system $K_xBi_{1-x}BiO_3$ the possibility of the partial substitution of Bi by rare earth ions via electrochemical synthesis has been reported recently (7). In order to check whether similar reactions are accessible in the lead system we performed an electrochemical experiment at 400 °C in open alumina vessel with the addition of terbium oxide $Tb_4O_7$ to the melt system. The reaction leads to the anodic deposition of black cubic crystals. According to microprobe cation analysis the crystals contain K, Ba, Tb and Pb. The X-ray pattern could be indexed with a simple cubic perovskite cell (table 1). We conclude that this phase represents a member of the solid solution $K_xBa_{1-x}Tb_yPb_{1-y}O_{3-z}$ similar to the cubic bismuth phases $K_xBa_{1-x}(RE)_yBi_{1-y}O_{3-z}$ systems reported earlier (7).

FIG. 2

Resistivity curve for a single crystal of $K_xBa_{1-x}PbO_{3-y}$ obtained by electrochemical preparation.

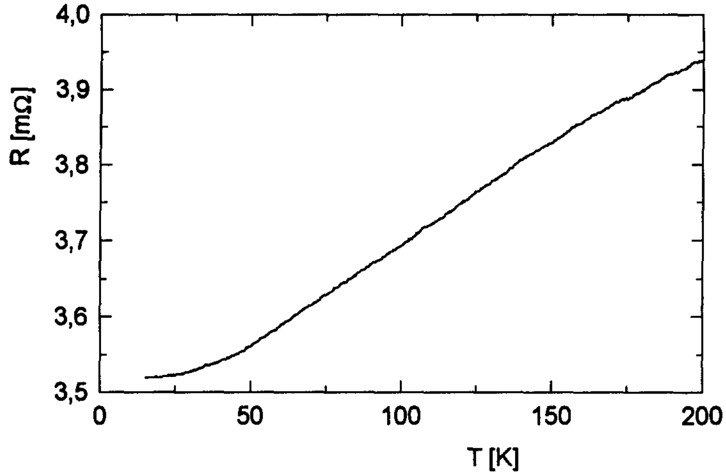
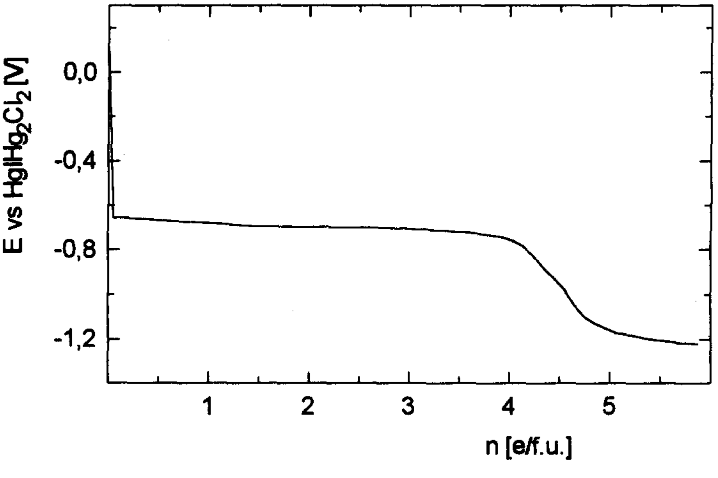


FIG. 3

Electrochemical reduction of $Ka_{0,2}Ba_{0.8}PbO_{3-y}$ in 1 M aqueous KOH at ambient temperature: potential versus charge transfer n ($e^-$/formula unit).



In an investigation on the electrochemical reactivity of BaPbO and $K_{0.2}Ba_{0.8}PbO_{3-y}$ in aqueous electrolyte (1M KOH) we found that both phases can be reduced directly to lead metal according to the scheme given in eq. 1.

$$BaPbO_3 + 3\,H_2O + 4e^- \rightarrow Pb^o + Ba^{2+} + 6\,OH^- \qquad (1)$$

In fig. 3 the potential/charge transfer diagram is given for this process. The reaction proceeds in a two phase system at ca. - 700 mV vs standard calomel electrode. The observed charge transfer is slightly higher than the calculated value which is most likely due to the discharge of minor amounts of hydrogen as an electron consuming side reaction. Experiments on the anodic oxidation of the K phase under identical conditions yielded no evidence for the presence of hydroxyl groups with mobile protons that could be removed by topotactic electron/proton transfer (11).

## Conclusions

The results described demonstrate that the chemical and electrochemical synthesis of ternary and quinquinary oxoplumbates from alkali hydroxide melts represents a useful and variable low temperature technique for the preparation of these perovskite materials. The investigation on single crystals demonstrate, however, that compositional inhomogeneities occur which can only be avoided by rigid control of the reaction parameters involved. The alkali substituted phases turned out to be reduced components with PbII/PbIV mixed valence. The problem whether the charge balance in these phases is achieved via defects in the anion sublattice or by partial protonation of lattice anions (incorporation of hydroxyl groups) requires neutron diffraction and H-NMR studies.

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