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Anodic Synthesis and Characterization of Na-Pb-O, Na-Pb-Bi-O Crystals

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Abstract: Crystals of Na-Pb-O and Na-Pb-Bi-O were electrosynthesized on the anode from molten salts. The resulting crystals have a hexagonal structure, in which the base ions (Pb and Bi) are in high oxidation states. By using KOH/NaOH (atomic ratio K:Na=1:1) mixture as a flux, incorporation of K ions into the lattice is inhibited while incorporation of Bi ions is enhanced. The magnetic measurement shows that the Na-Pb-Bi-O crystals are dominated by diamagnetism.

Keywords: Lead complex oxides, anodic electrosynthesis, crystal growth, chacacterization.

Since the discovery of high-T_c oxide superconductors in the late 1980s, many scientists have been greatly motivated to synthesize novel complex oxides. The popular method for synthesis of complex oxides has been solid-state chemical reaction. This method, however, has its limitations such as high synthetic temperatures, inhomogeneous reactant mixing and poor product purity, *etc*. To overcome these disadvantages, an anodic electrosynthesis technique, first developed by Norton[1], has been used to prepare crystals of complex oxides from hydroxide flux. This technique is in particular suitable for preparation of temperature sensitive, highly oxidized and electrically conducting complex oxides. Because the hydroxide flux melts at relatively low temperature and stabilizes highly oxidized species, and the electrochemical process selects only the most conductive phases while electrodeposition of insulating phases is self-limited. However, complex oxides obtained directly by electrodeposition from molten salt are uncommon, most of the complex oxides can not deposit on the anode. To our knowledge, so far only several Bi-based[1-4] and Cu-based[5-8] complex oxides have been electrodeposited on the anode from molten salts successfully. To find new complex oxides electrodeposited on the anode becomes more and more difficult, but effort of synthesis of complex oxides with this technique has not been exhausted. In this letter we report the anodic electrodeposition of Na-Pb-O (NPO) and Na-Pb-Bi-O (NPBO) crystals in KOH/NaOH fluxes at temperatures less than 300℃. The resulting deposits are characterized by using XAM, SEM, XRD, XPS and magnetic measurement. To our knowledge, it is the first example to synthesize these complex oxides through anodic deposition route.

NPO and NPBO crystals were electrodeposited on the anode from KOH/NaOH fluxes. The reaction mixture for NPO consisted of 40 g of KOH, 24 g of NaOH, 8 g of

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$Pb(NO_3)_2$ and 1 g of ZnO. The melt for NPBO consisted of 40 g of KOH, 24 g of NaOH, 4 g of $Pb(NO_3)_2$, 2.8 g of Bi_2O_3 and 1 g of ZnO. The reactants were in analytical grade, in which KOH contained *ca.* 13% water and 2% NaOH by weight as received from the manufacturer. ZnO was used as an easily reduced sacrifical reductant. For preparation of each sample, the starting materials were loaded into a telflon crucible and melted at 270 ℃-280℃ in air. The lowered melting point is presumed due to the high water content of commercial KOH, exposuring in atmosphere. One hour later, the melt was stirred and then two electrodes were inserted into the solution. The anode was a 1 mm-diameter Pt wire and the cathode was a Au wire. Electrodeposition was carried out by constant-current electrolysis under stationary conditions for 22 h. The cell current was 5 mA and the current density was about 27 mA/cm^2. Black oxide crystals were grown on the anode. The crystal growth was repeatable.

The morphology of the anodic NPBO crystals is shown in **Figure 1**. The morphology of NPO is very similar to that of NPBO. The SEM image indicates a granular electrodeposition. XAM was used to analyze K, Pb, and Bi contents in the crystals. Since XAM may not be suitable for determining Na, the Na content was estimated by XPS analysis. The chemical compositions, as determined by XAM and XPS, are $Na_{1.1}Pb_{1.0}O_x$ for NPO and $Na_{3.6}Pb_{0.82}Bi_{0.18}O_y$ for NPBO. It is interesting to note that K ion was not incorporated into the crystals in such mixing flux whose K/Na atomic ratio was 1/1. We have carried out another experiment, in which the starting materials were similar to those of NPBO, except that the mole ratio of KOH/NaOH was 30/1. The composition of the resulting crystals was $K_{0.3}Na_{0.4}Pb_1Bi_{0.02}O_z$, in which the Na concentration is about 40 times larger than that in the bath. These results indicate that the anodic deposition is in favor of the migration of the sodium ion towards the growing electrode and the insertion of the sodium ion into the crystal lattice. It also can be concluded that incorporation of Bi atoms is significantly enhanced by using mixed KOH/NaOH flux instead of single KOH flux, implying that the intrinsic difference of electrochemical oxidation ability between KOH and NaOH may significantly impact the deposition mechanism.

Figure 2 shows the XRD patterns for NPO (a) and NPBO (b). It can be seen from the **Figure** that there is little difference in the peak positions of a and b. We have searched the corresponding oxides in the starting materials and the related oxides with the XRD database, and no match has been found. Therefore, the diffraction patterns of the crystals were indexed using TREOR[9]. The indexing results are quite good and the figures of merits were M(16)=93, F(16)=52 for NPO and M(13)=39, F(13)=15 for NPBO. After least square refinement and unit cell reduction, the crystals were both indexed as hexagonal with a = b = 3.3045 Å, c = 16.5444 Å for NPO and a =b = 3.3239 Å, c = 16.5763 Å for NPBO.

The $Pb4f_{7/2}$ and $Bi4f_{7/2}$ binding energies for NPBO, determined by XPS, are 137.3 eV and 158.2 eV, respectively. It has already been recognized that the binding energy of Pb(Ⅳ) in conducting oxides (137.4 eV) is lower than that of Pb(Ⅱ) in insulating oxides (138.2 eV)[10]. Atoms with higher oxidation state have a lower electron binding energy, this anomaly has been attributed to the effect of conductivity on extra-atomic relaxation[11], which is the same with Bi ions. Therefore the Pb and Bi valences have been assigned to

Figure 1 SEM image of the anodic crystals NPBO

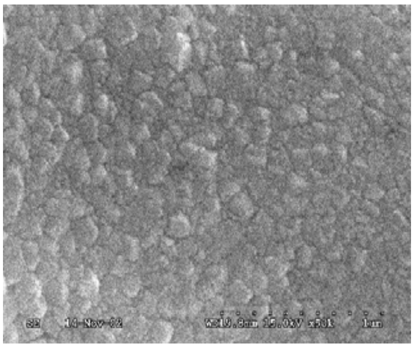
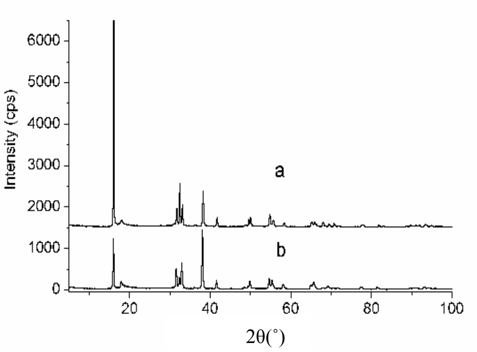


Figure 2 XRD pattern of a) NPO and b) NPBO



Pb(IV) and Bi(V), respectively. In fact high oxidation states for Pb and Bi in the crystals are predictable because of the highly oxidizing conditions created electrochemically in KOH/NaOH flux at the anode. Besides, the Pb4f and Bi4f peaks are quite narrow and symmetric, indicating that there is no evidence for existence of the mixed valence for both Pb and Bi ions.

The curve of magnetic moment *versus* temperature for NPBO shows that the oxide is not superconducting but diamagnetic. Since superconducting oxides, including $BaPb_{1-x}Bi_xO_3$, have perovskite type structures, it is predictable that the NPBO oxide with hexagonal structure is not superconducting.

In summary, crystals of NPO and NPBO complex oxides have been prepared using the anodic crystallization method from molten salts. The resulting crystals have a hexagonal structure. By using KOH/NaOH mixture as flux, incorporation of K ions is inhibited while incorporation of Bi atoms is enhanced. Temperature sensitive and highly oxidized complex oxides are difficult to prepare. Present method can solve these problems. This method offers the advantages of low temperatures and simplicity in the growth of crystals of highly oxidized complex oxides, so it can solve the problems in preparing temperature sensitive and highly oxidized complex oxides.

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