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$KTaO_3$ powders and thin films prepared by polymeric precursor method

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Abstract

This work presents perovskite-type $KTaO_3$ powders and thin films synthesis, using a low-cost route based on Pechini method. Powders and films were studied by X-ray diffraction, energy dispersive spectroscopy and scanning electron microscopy. Pyrochlore-free samples are achieved at moderate temperatures (650 °C). Nevertheless, it was verified that with temperature increasing, a small amount of secondary perovskite phases, presenting lowered lattice parameters, is formed in powders. These phases are attributed to stoichiometric deviation due to K losses during thermal treatment. The EDS results support this hypothesis. The microstructure of a sample annealed at 625 °C was studied by X-ray line-broadening analysis. The sample contains a negligible amount of structural distortions and the crystallites are on average isotropic. Concerning $KTaO_3$ films, it was observed that substrates play an important role. While the films prepared onto sintered alumina substrates present pyrochlore contamination, films prepared onto (100) $SrTiO_3$ and (100) $LaAlO_3$ are single phased (only perovskite phase is present) and highly oriented. $KTaO_3$ is epitaxial onto (100) $SrTiO_3$ and textured onto (100) $LaAlO_3$. Moreover, films are crack-free and homogeneous. Refractive indexes, measured by ellipsometry, are about 1.95 and the film thickness is in the range of 130 nm per layer.

Keywords: $KTaO_3$; Polymeric precursor method; Powder X-ray diffraction; Diffraction line-broadening analysis; Thin films

1. Introduction

$KTaO_3$ (KT) is a cubic material presenting two possible forms: the pyrochlore $K_2Ta_2O_6$ phase which is formed at low temperatures and the perovskite $KTaO_3$ phase which is formed at moderately high temperatures. Presenting an incipient ferroelectricity and the possibility of doping with several elements, KT is suitable for fundamental studies and presents some potential applications.

Less studied than other perovskites, KT is an insulator in the stoichiometric form, and becomes a n-type semiconductor when it is ion or defect-doped. In the semiconducting form, it could be used as high-temperature gas sensors and fuel cells [1]. Ca and M ($M = \mathrm{Co}, \mathrm{Mn}$) co-doping produces a ferromagnetic behavior, that transforms this material in a promising candidate for colossal magnetoresistance applications [2]. In the solid solution with Nb ($KTa_{1-x}Nb_xO_3$), it is of first interest for tunable microwave devices [3]. Moreover, it appears, beside $BaTa_2O_6$, as a good alternative material for photocatalytic purposes [4]. Finally, mixed oxides like $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ can be useful for holographic and pyroelectric devices [5].

Despite its potential applications and the relatively numerous studies, KT preparation is not trivial. Problems related to stoichiometric deviation, due to K losses, and to pyrochlore–perovskite phases control are frequently reported [6]. Several approaches are proposed to avoid these problems with more or less efficiency. In fact, KT synthesis is still an open issue, specially when it concerns the growth of high quality oriented films. In this frame, this work proposes the preparation of KT powders and thin films using a simple and not expensive chemical route derived from Pechini method [7]. Chemical routes are very well known to allow the formation of stoichiometric, contaminant-free and reduced particle sized materials at low temperatures (which reduces the losses of volatile elements during calcination step)—so it is believed to be appropriated for the $KTaO_3$ and related compounds preparation [8].

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2. Experimental

The first step in KT ($a = 3.988$ Å, ICDD PDF2 No. 77-1133 [9]) synthesis was the resin preparation that was carried out according to the polymeric precursor method. The starting materials were potassium carbonate (Fluka, 99%) and tantalum ethoxide (Strem). The tantalum ethoxide was dissolved in a water-free ethylene glycol/citric acid solution in order to avoid its hydrolysis. The subsequent addition of ethylenediamine (for pH adjustment) results in a limpid and precipitate-free dark brownish solution. Then, an aqueous potassium citrate solution was added and the temperature was kept at 90 °C to promote the polymerization. At this step, the addition of water does not disturb the solution stability. In this synthesis, an excess of potassium (K/Ta = 1.25, in mol) was used to compensate subsequent K losses. The citric acid/metal ratio (CA/M, in mol) and citric acid / ethylene glycol ratio (CA/EG, in weight) were fixed at 3 : 1 and 40 : 60, respectively.

The next step was the viscosity adjustment by water evaporation or addition. The viscosity, measured with a Brookfield viscometer, was fixed at about 25 cP [10]. In case of thin films preparation, the substrates were ultrasonically cleaned with alcoholic or hot surfactant bath. The first type of cleaning was used for Al_2O_3 (sintered alumina) substrates and the second one for single crystal $SrTiO_3$ and $LaAlO_3$ ones. All substrates were rinsed with distillated water and isopropanol and finally dried in hot air flow. Films were prepared by dip coating (home made device), dipping and withdrawing stages were carried out at a fixed rate of 1.0 cm min^{-1}. Wet films were then submitted to two thermal treatment cycles performed under air: (i) 300 °C for 4 h using heating and cooling rates of 5 °C min^{-1} (to eliminate organic matter) and (ii) in the range 500–800 °C for 1 h using heating and cooling rates of 5 °C min^{-1} (for crystallization).

In the case of powder preparation, the resin was submitted to the same thermal treatment cycle. After the first calcination (300 °C for 4 h), the pyrolized polymer was de-aggregated in agate mortar and then submitted to the second calcination step (crystallization).

The samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive spectroscopy analyses (EDS) and ellipsometry. The XRD patterns of powders and polycrystalline films were routinely recorded with a powder diffractometer INEL CPS 120, using $Cu_{K\alpha 1}$ radiation ($\lambda = 1.5406$ Å), fixed incident angle (approximately 8°) and a curved position sensitive detector (setup A). For some powders, high-quality X-ray powder diffraction data were also collected at room temperature with a Siemens D500 diffractometer, equipped with an incident-beam germanium monochromator ($Cu_{K\alpha 1}$ radiation, $\lambda = 1.5406$ Å) and whose characteristics have been described elsewhere [11] (setup B). The diffraction patterns of all nanocrystalline $KTaO_3$ samples were scanned over the angular range 20–60° (2θ). For the microstructural analysis, the powder pattern of a $KTaO_3$ sample annealed at 625 °C ($\mu = 909$ cm^{-1}, where μ is the linear absorption coefficient calculated with the $Cu_{K\alpha 1}$ radiation) was scanned over the angular range 20–145° (2θ), with steps of 0.015° and 50 s counting time per step. Instrumental line profiles were obtained with the NIST standard reference material SRM660a LaB_6 whose linear absorption coefficient is close to that of $KTaO_3$ ($\mu = 1138$ cm^{-1}). The positions and line profile parameters (full width at half maximum FWHM, integral breadth β and line profile shape) of the individual reflections of LaB_6 and $KTaO_3$ samples were obtained with the fitting program PROFILE available in the software package DIFFRACT-AT supplied by Bruker AXS. Indexing of the powder patterns was performed with the program DICVOL04 [12]. For the single-line microstructural analysis, the modelling of the instrumental profiles was carried out as described elsewhere [13] and, for the whole pattern fitting approach, with the profile fitting facility implemented in WinPLOTR [14]. The microstructure analysis of the $KTaO_3$ sample annealed at 625 °C was carried out from X-ray diffraction line-broadening analysis based on the whole pattern fitting technique by means of the program FULLPROF [15]. In this approach, the integral breadths of the individual Bragg reflections are derived from a pseudo-Voigt approximation to separate apparent volume-weighted size ε_β and microstrain e. The traditional Voigt/Langford method was also applied. The method is based on the integral breadth [16] associated with the pattern decomposition technique using a Voigt function [17]. The observed integral breadths are corrected for the instrumental contribution to obtain the integral breadth in reciprocal units β^* ($= \beta_{2\theta}\cos\theta/\lambda$). If line broadening is solely attributed to a size effect, the volume-weighted apparent size ε_β ($= \beta^{*-1}$) is obtained. In contrast, if structural distortions also contribute to line broadening, the separation of the different effects is based on the assumption that the 'size' and 'strain' profiles are Lorentzian and Gaussian, respectively. If line broadening is isotropic, as found here, 'average' size-strain plots $(\beta^*/d^*)^2$ versus $\beta^*/(d^*)^2$, introduced by Langford [16], can be used. The intercept and the slope are related to the distortions e and the apparent size ε_β, respectively.

The patterns of the oriented films were obtained with a 4-circles diffractometer (Brüker AXS D8 Discover), using the $Cu_{K\alpha}$ radiation and giving access to the theta–2theta, rocking curve (omega-scan) and phi-scan measurements. EDS analysis was performed on graphite coated pellets using optimized experimental conditions (10 kV as accelerating voltage and 10 nA as beam current), using a Jeol JSM 6400 microscope equipped with an ISIS Oxford analyzer). SEM observations were carried out in a JSM 6301F Field Emission Scanning Microscope, working at low voltage (9 kV), so no metallization was required for microstructure observation. Ellipsometric measurements were performed using a He–Ne laser beam ($\lambda = 632.8$ nm) with an incidence angle of 70° to the normal of the sample (Jobin Yvon, Ellisel software).

3. Results and discussion

3.1. KT powders

3.1.1. Phase analysis

The KT powders were obtained by the resin calcination and were characterized by XRD and EDS. Using a routine