Structure Solution of $NaYO_2$ Compound Prepared by Soft Chemistry from X-Ray Diffraction Powder Data.

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In this work we reveal the structure of a $NaYO_2$ compound solved from the X-ray diffraction powder pattern using the "ab-initio" structure solution approach. The compound turned out to be of trigonal structure, S. G. R-3m isomorphous with α-$NaFeO_2$ layered compound. The lattice parameters are a = 3.404 and c = 16.602 Å, respectively, the atoms being located in Wickoff sites (cba) for O, Na and Y, respectively, leading to a calculated density of 4.31 g/cm^3. The ordering of sodium and yttrium atoms into alternate (111) planes of the cubic close-packed oxygen lattice of $NaYO_2$ is very regular. The octahedra are slightly distorted, the positive deviation of the O_z parameter from 0.25 elongates the NaO_6 octahedra while compressing the YO_6 octahedra. Actually the Na-O and Y-O bond distances are 2.58 (1) and 2.25 (1) Å, respectively, as it is expected from their ionic radii values reported (1.16 vs 1.04 radii for both ion-species octahedral coordination). Finally, the Na-Y, Y-Y, and Na-Na next neighbor distances are close to 3.40 Å.

1. Introduction

Even nowadays, relatively little is known concerning the synthesis of ternary, $A_XM_YO_Z$, or even polynary oxides, for example $A_XB_WM_YO_Z$, of the lanthanides and/or 4d transition elements (M) with alkali metals (A,B,..), despite the considerable efforts which have already conducted to innumerable applications of such materials in the technological field of photoluminescence and optics.
In the latter '70 a scientific work (Brunn and Hoppe, 1977) reported unknown cubic forms of $NaScO_2$ (a = 4.52_5 Å), $NaYO_2$ (a = 4.79_1 Å), $NaDyO_2$ (a = 4.80_0 Å), $NaTmO_2$ (a = 4.74_3 Å), $NaYbO_2$ (a = 4.73_0 Å), $NaLuO_2$ (a = 4.71_5 Å). Solid state reactions at high temperature were conducted by heating mixtures of the binary oxides AO_X (A = Na, K, Rb, Cs) with active forms of M_2O_3, respectively. We note that such oxides are almost absent for the 4d transition metals with the only exceptions of Y and Sb. Compounds with general formula AMO_2 (A = alkali metal, M = transition metal) are currently being investigated (Zhao et al., 2011) after solid state syntheses for their optoelectrical properties. Despite the efforts to understand the existence of cubic forms for such ternary phases -the powder data Brunn & Hoppe were interpreted in terms of a statistical distribution of cations with different charge and ionic radius- it turns out that very few structures are retrieved from the modern, updated crystal data base ICSD and COD. Actually, simple cards of powder diffraction intensity vs 2θ lines, for some of the compounds studied by Brunn & Hoppe, as well as their densities are reported in the ASTM data base, but the space group sometimes is missing. One of the main problems is that reliable single-crystal data are almost non-existent (Favre-Nicolin and Cerny, 2002). As a matter of fact, the growth of single crystals was achieved only sporadically for reasons ascribable to the high melting points of the lanthanide oxides, M_2O_3, and the relatively high vapor pressures of the alkali-metal oxides, A_2O (A=Li-Cs). Alternatives using soft chemistry synthetic multistep techniques (Blakely et al., 2014) were proposed and successfully applied in the last 20 years in the magnetic and optics field, which expanded considerably for the production of doped powdered garnets in competition with single crystals. Nevertheless the synthesized products were invariably under the form of powder. On

the other hand, the widespread availability of powerful personal computers combined with advanced crystallography programs for interpretation of data coming from high-resolution commercial powder diffractometers have increased the successful solution of relatively complex structures (so-called ab-initio methods). During the course of a relatively simple synthesis of Y_2O_3 powders we have observed a by-product of chemical composition Na, Y and O, whose powder pattern can be solved satisfactorily with the Rietveld method (Rietveld, 1967, Rietveld, 1969) as the sum of two contributions, the smaller from well-known Y_2O_3 cubic structure, space group Ia-3 and the larger from $NaYO_2$ compound according to the R-3m symmetry. We report here our steps for solving the structure of $NaYO_2$ and discuss the differences with previous partial solutions which were proposed by Brunn and Hoppe.

2. Experimental and methods

Yttrium Nitrate (99.9%) and NaOH (>97%) were purchased from Sigma Aldrich Ltd Ltd. (Japan) and used without further purification. In a typical synthesis process, 1 g of yttrium nitrate, 3 g of NaOH and 20 mL of distilled water were put into a 25 mL Teflon-lined autoclave. The autoclave was sealed, heated in an electric oven to 200 °C with agitation and maintained at this temperature for 6 h with rotation. Then it was cooled to room temperature by air quenching. The precipitate was washed with distilled water and dried at room temperature. Finally the compound were thermally treated at 500 °C for three hours.

2.1 X-ray powder diffraction
Structural investigations were performed using a Rigaku D-IImax X-ray powder diffractometer in Bragg-Brentano geometry with Cu Kα radiation (λ = 1.54178 Å). The X-ray generator worked at a power of 40 kV and 30 mA and the resolution of the instrument (divergent and antiscatter slits of 1°) was determined using LaB_6 standard (SRM 660a) free from the effect of reduced crystallite size and lattice defects (Enzo et al., 1988). The powder was spread onto a scotch tape and the pattern was recorded in the angular range 10°–120° in 2θ, with a step scan of 0.05° and counting time of 5 s per point.

Peak location was conducted using the X'Pert Highscore Program (PANalytical, 2003)and the indexing step using the McMaille (Le Bail, 2004) software supplemented with DICVOL06 (Boultif and Louer, 2004) and N-TREOR (Altomare et al., 2000) programs. Direct-Space Methods(Cerný and Favre-Nicolin, 2007) were adopted in order to locate the atoms inside the unit cell. The simulated annealing program, Endeavour [Brandenburg and Putz (2014), Putz et al., (1999)] was employed. In addition to this, a parallel approach was carried out using FOX (Favre-Nicolin and Cerny, 2002), and MAUD programs (Lutterotti, 2014), and (Lutterotti, 2010) .

Rietveld refinement was performed using MAUD software (Lutterotti, 2014) and crystal structure visualization using DIAMOND (H. Putz and Brandenburg, Crystal Impact - 2014) program.
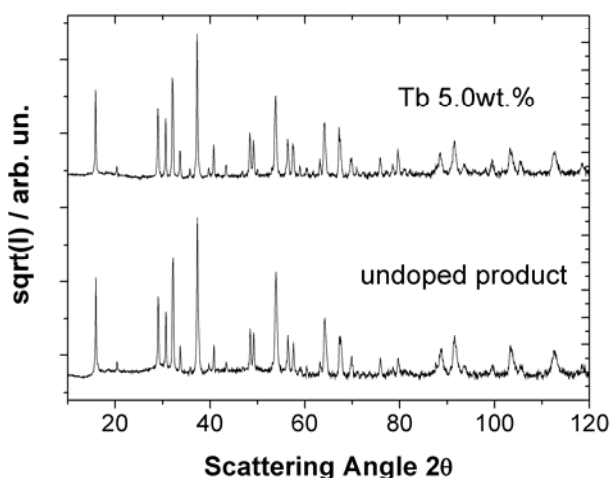.

3. Results and discussions

Figure 1. The powder XRD of the two indicated products showing several unattributed peaks due to new phase(s).

Figure 1 shows the diffraction pattern of square root intensity vs. 2θ of the two specimens synthesized. The patterns look very similar, suggesting that doping of 5% wt. Tb is not affecting the final distribution of products.
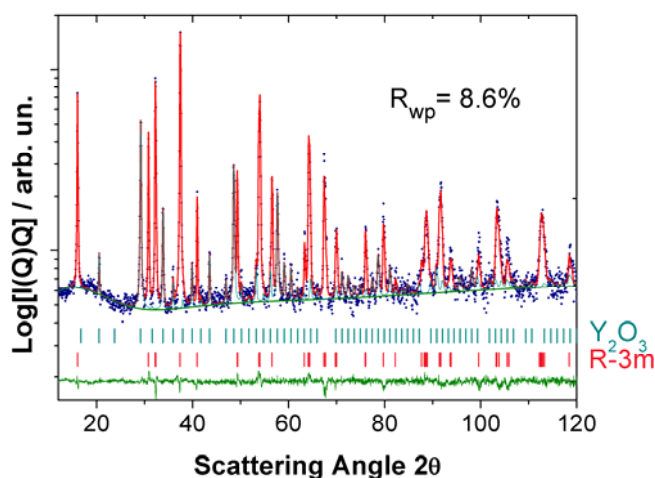

Figure 2. The Rietveld fit (full line) to the experimental data (points) after solving the sequence of peaks not belonging to cubic yttria. The bar sequence in red pertains to the space group R-3m. The curve at the very bottom refers to the residuals.

A quick analysis using the automatic search-match program X'Pert suggests only a minor presence of cubic Y_2O_3 contrary to our expectations. A concomitant analysis by X-ray fluorescence revealed the presence of sodium in a non-negligible quantity, likely deriving from NaOH precursor. Apart from yttria the program returned a list of cubic oxide phases with lattice parameter a ≈ 4.80 Å and presumed space group Fm-3m, as it was reported by Brunn & Hoppe (1977). Despite of this, the peak attribution list remained uncompleted, leaving the two patterns shown in Figure 1 essentially unresolved. Adopting an orthodox approach for indexing by using McMaille (Le Bail, 2004), we determined easily lattice parameter values a = 3.404 and c = 16.602 Å in the hexagonal setting, respectively, i. e., cell volume of 166.7 Å^3. Such values were further confirmed with DICVOL06 (Boultif and Louer, 2004). Assuming the existence of $NaYO_2$ stoichiometric composition based on the oxidation state of elements, three formula units in the elementary cell lead to a calculated density of 4.31 g/cm^3, certainly different from the experimental figure of 4.20 g/cm^3 measured by Brunn and Hoppe but slightly lower than the value of 4.34 g/cm^3 calculated on the basis of their approximate structure determination. Loading Endeavour with the stick pattern, after input the cell in the hexagonal setting, the best space group was determined to be R-3m on the basis of systematic absences and the atoms were quickly located in Wickoff sites (cab) for O, Y and Na, respectively. Apart from the two lattice constant parameters, one further positional parameter is necessary for oxygen sites 6c (00,z), where z = 0.267. This allows describing fully the experimental pattern as it is shown in Figure 2.

The Rietveld refinement conducts to 20 wt% of the Y_2O_3 cubic phase (S. G. Ia-3, lattice parameter a = 10.605 ±0.002 Å) and 80% of the new $NaYO_2$ phase, final refined parameters a = 3.405±0.001 Å, c = 16.601±0.002 Å. It is interesting to note that this structure is isomorphous with several intercalation compounds available from the ICSD archive such as α-$NaFeO_2$ and $NaSnS_2$, as reported by Orman and Wiseman, 1984) and Le Blanc and Rouxel, (1972), , respectively. The unit cell lattice parameters of the above mentioned phases are a = 3.022 Å; c = 16.082 Å and a = 3.69 Å and c = 25.54 Å for α-NaFeO2 and $NaSnS_2$ respectively and their calculated density d is 3.34 and 3.40 g/cm^3 respectively, not so different from our value assumed to fit into the unit cell volume. The ordering of sodium and yttrium atoms into alternate (111) planes of the cubic close-packed oxygen lattice of $NaYO_2$ is very regular (see figure 3). The octahedra are slightly distorted, the positive deviation of the O_z parameter from 0.25 elongates the NaO_6 octahedra while compressing the YO_6 octahedra. Actually the Na-O and Y-O bond distances are 2.58 (1) and 2.25 (1) Å, respectively, as it is expected from their ionic radii values reported (1.16 vs 1.04 radii for both ion-species octahedral coordination). Finally, the Na-Y, Y-Y, and Na-Na next neighbor distances are close to 3.40 Å.

It was previously noted that layered ordering is favored by a large difference in the ionic radii R of A^+ and M^{3+} where an ionic radii ratio R_M/R_A o 0.86 is typical for ordered phases. (Schougaard et al., 2006). In particular it was reported that the elastic energy associated with ions of different sizes stabilize M^{3+} and A^+ ordering into alternate layers (Wu et al., 1998). Our radii ratio of 0.90 should be at the borderline of such empirical rule. It should be pointed out that Bruesch and Schuler (1971) have reported the Raman spectra of twelve $NaBX_z$ compounds, which crystallize in the α -$NaFeO_2$ structure, namely B = Cr, In, Er, Ho, Y, Yb, and X = O, S. Adopting a simple force model for the Raman active normal modes, the repulsive forces between the vibrating anion layers were calculated and correlated with the structural parameters of the crystals. Among such dozen they reported also $NaYO_2$ which was estimated with space group R-3m, a = 3.386 Å and c = 16.43 Å respectively, while z = 0.26 and the distance between nearest anion layers d = 2.32 Å. The data turn out to be slightly different with respect to our X-ray determination. For sure the structure condition of our specimen is metastable since the initial biphasic ratio of un-doped specimen Y_2O_3/ $NaYO_2$ of 1:4 turned out to be reversed 4:1 after heating the powder at 700 °C for two h, the structure parameters of the R-3m phase being the same (see blue curve in Figure 4).

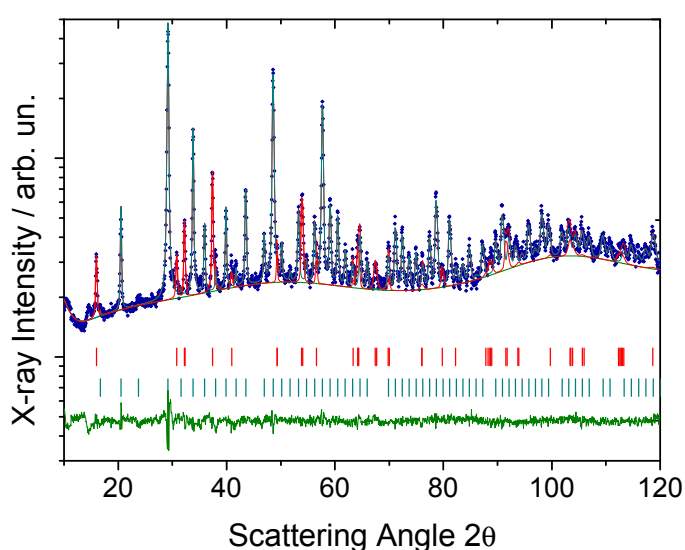*Figure 3. The Rietveld fit of the specimen heated at 750 °C for 2 h. The new layered compound (red line) appears decreased while the yttria phase becomes dominant.*

Recently. (Porthault et al., 2012) have conducted a spectroscopic and diffractometric study of the (Fd-3m)-to-(R-3m) transformation process as a function of the temperature, involving $LiCoO_2$ powders obtained single-phase by sol/gel process involving acrylic acid as a chelating agent. We have examined the possibility that our patterns in Figure 1 are ascribable to a higher Fd-3m space group symmetry by assuming a cubic lattice parameter of 9.60 Å, i.e., twice the value assumed by Brunn & Hoppe. The cell volume of 887.5 $Å^3$ could host a total of 16 stoichiometric units with Wickoff sites edc for O, Y and Na, respectively. The relative intensities of the peaks were determined "rather well" using just one positional parameter of the triplet (x,x,x) relevant to 32(e) sites. However, such empirical description of the diagram, while involving just the a-axis lattice and the x positional parameter, expected to further improve our control of the experimental pattern, it is not completely satisfactory. Particularly few peaks with evident asymmetry remained difficult to account properly in a precise 2Ө location list beyond experimental uncertainty, (see top pattern of Figure 5 a, b, c and d, respectively). Considering also the better agreement factors in describing the experimental pattern, we reject the occurrence of a cubic structure, and conclude that the R-3m space group is supported also by powder X-ray diffraction.
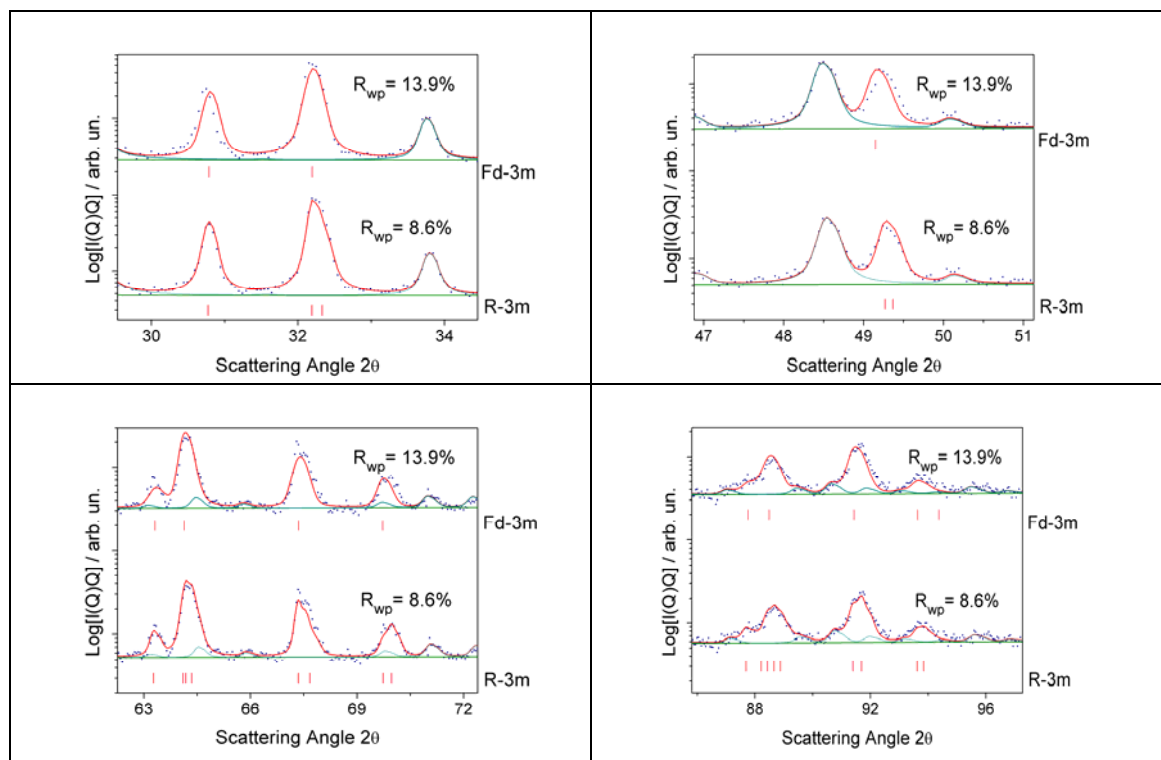
Figura 4. Specific angular ranges selected to verify the pertinence of the R-3m (lower curves) vs Fd-3m (upper curves) model in accounting for the experimental data. It is concluded that the cubic model is inadequate to solve satisfactory the experimental data.

4. Conclusions

We have solved the structure of a new $NaYO_2$ layered compound, rhombohedral with space group R-3m, normally known at equilibrium with the monoclinic habit. The lattice parameters determined after Rietveld refinement of a mixture of 20 wt.% cubic yttria and 80 wt.% of the new phase are a = 3.404 and c = 16.602 Å, respectively, the atoms being located in Wickoff sites (cba) for O, Na and Y, respectively, leading to a calculated density of 4.31 g/cm^3. Both Na^+ and Y^{3+} cations are surrounded by Oxigen atoms in a distorted octahedral environment on account of their different ionic radii. In perspective we have the possibility to explore the thermal stability of the phase on increasing the temperature and to verify the possible polymorphic forms of such compound by selecting the chemical environment during preparation throughout soft chemistry.

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