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Preparation of $NaIn(WO_4)_2$ nanocrystals and a charge for crystal growth *via* the free-of-rubbing mechanical activation of the Na_2CO_3–In_2O_3–WO_3 system

Farit Kh. Urakaev

V. S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 333 2792; e-mail: urakaev@igm.nsc.ru

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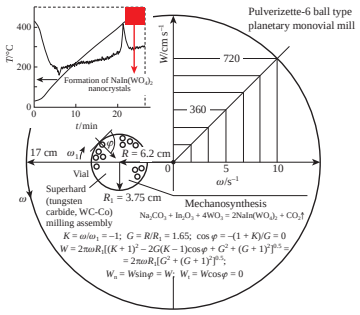
The pollution-free or free-of-rubbing mechanical activation of the Na_2CO_3–In_2O_3–WO_3 system resulted in the formation of the nanosized crystallites (nanocrystals) of $NaIn(WO_4)_2$ at 698 K (425 °C). The use of very hard milling tools of mechanochemical reactors allows one to offer also a new way of charge preparation with a composition and structure suitable for growing the bulk crystal of $NaIn(WO_4)_2$.



Double tungstates, in particular $NaIn(WO_4)_2$, are of interest as scintillators and laser hosts due to the large absorption cross sections of rare-earth ions in these lattices.[1–3] For example, undoped $NaIn(WO_4)_2$ shows the most promising scintillation characteristics at room temperature. In addition, the In:$NaBi(WO_4)_2$ crystals are characterized by high density and radiation resistance, which is of interest in quantum electronics, acoustooptics, and high-energy physics (neutrino detection).[2,4]

Mechanochemical methods based on mechanical activation (MA) are very efficient in producing different compounds,[5] including oxide systems.[6,7] Despite their high efficiency in various fields,[8–11] mechanochemical methods are hardly ever used for synthesizing substances intended for use as bulk crystals only.[12–14] If a milling assembly, including milling media and parameters, is carefully selected, it is possible to obtain large amounts of powders with accurate control of particle and crystallite sizes and the amount and types of defects and impurities.[15] Prolonged milling in high-energy mills is necessary for obtaining nanoparticles, but it leads to the contamination of starting materials.[16] Since the milling process tends to contaminate powder, it can be used as an additional route for introducing a milling assembly material as a desired reagent or dopant into a powder.[17] Diamond abrasive[18] and milling[19,20] tools are high performance ultrahard materials, which have high hardness, excellent abrasion resistance, and good thermal conductivity. Due to these properties, diamond abrasive-reactive tools have been increasingly applied in machining and other industries.

Another aspect of MA is related to growing interest in nanoscopic systems based on rare-earth metals.[21–23] It was shown earlier that the particles of substances processed in mechanochemical reactors are subject to abrasive-reactive wear on a nanosized scale.[24,25] Consequently, when the Na_2CO_3–In_2O_3–WO_3 system is subjected to MA, nanosized precursors are likely to be formed during double tungstate synthesis in this system.

High-energy (*e.g.*, planetary, see Figure 1) mills are used to perform MA.[16,26–30] The most significant MA parameter in a ball-type planetary mill is relative velocity W of the interaction of milling tools (the balls and drum walls). If R and R_1 are the radii between the rotation axes and of the drums, ω and ω_1 are the frequencies of rotation of the carrier (our mill radius is 17 cm) and drums, respectively (and are opposite to each other, as a rule). $G = R/R_1$ is a geometrical factor; $K = \omega_1/\omega$ is a kinematic factor, where ω and ω_i are the angular rotation velocities (for our mill, $|\omega| = |\omega_1| = 2\pi\omega$), φ is the ball's angle of separation, and $\cos\varphi = (1 + K)/\Gamma$ is the condition of a ball leaving the wall. Then,[25,31,32] the values of W and its normal (W_n) and tangential (W_t) constituents are given in Figure 1. During the collisions of milling tools whose surface is coated by a layer of treated particles of powder,[33] short-lived (t) impulses of pressure (P) and temperature (T) or so-called t–P–T conditions arise upon contact

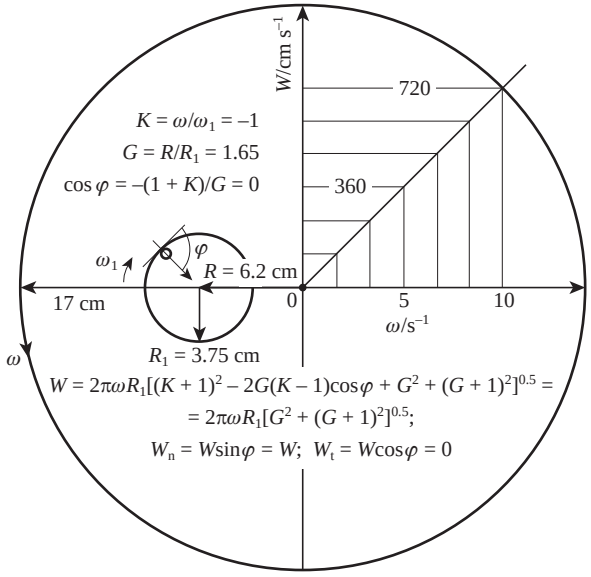


Figure 1 Geometry and kinematics of the Pulverisette 6 ball planetary mill.

as a result of impact-friction interaction.[34,35] The parameters of the *t*–*P*–*T* conditions govern both the degree and specificity of the MA reactions and their difference from those under routine *P*–*T* conditions.[35–37]

A Pulverisette 6 ball-type planetary monodrum mill was used for MA. Its equation (Figure 1) characteristics were R = = 6.2 cm, $G = R/R_1 = 1.65$, $K = -1$; consequently, $\cos\varphi = 0$ and $\varphi = 90°$. Drum and balls of a superhard material (tungsten carbide, 93% WC + 6% Co, ρ = 14.7 g cm^{-3}; Mohs hardness, 9; drum volume, 250 cm^3; ball diameter, 1 cm; and the number of balls, 50) were used. The numerical values of W for the drum are shown in Figure 1.

Applying the above milling assembly material, MA was conducted for powder mixture of the following stoichiometric composition and total contents (g) of the initial high purity reagents for the test MA reaction:

$$Na_2CO_3 + In_2O_3 + 4WO_3 = 2\,NaIn(WO_4)_2 + CO_2\uparrow;\ 13.108\ g. \quad (1)$$

MA processes in the carbonate systems are accompanied by the decomposition of carbonates with CO_2 emission.[35–37] This makes it possible (i) to accelerate the preliminarily thermal removal of CO_2 from the working mixture for growing crystals after the MA of the initial mixture and (ii) to perform gravimetric[16,38] or barometric[35,39] monitoring of the kinetics of MA reactions.

A regime of mechanical processing for (1) system was: (H) homogenization at ω = 100, 140 and 210 rpm; duration, 14×3 = = 42 min; weighing and sampling; (G) grinding at ω = 280, 350 and 420 rpm; duration, 14×3 = 42 min; weighing and sampling; (A) activation at ω = 490 rpm (14 min), at ω = 560 rpm (12 min) and ω = 600 rpm (10 min). In actual practice, the homogenization (H) and grinding (G) of the powder mixture take place at all employed values of mill revolutions, while activation (A) occurs only at high revolutions. Hence, the total time of the mechanical treatment of mixture (1) was 42 + 42 + 36 = 120 min.

As follows from the results of gravimetric measurements, the MA of materials with hardness of up to 6 on the Mohs scale does not lead to abrasion wear for the selected material of milling tools. The hardness of components in the test MA systems does not exceed 5. This made it possible to avoid abrasive-reactive wear and to study for the first time the pure influence of MA on the preparation of a charge.[16,17]

To evacuate the gaseous products of reaction (1), MA was performed without vacuum compression in the drum. The drum was weighed to within ±0.01 g before MA, during sampling and after MA. The drum weight was constant before sampling after (H) homogenization. The samples obtained after MA were studied by X-ray diffractometry (XRD), differential thermal analysis (DTA) and annealing in an air atmosphere.

$NaIn(WO_4)_2$ can be produced by several methods. For example, $NaIn(WO_4)_2$ was synthesized by the reaction[1] of stoichiometric mixtures of WO_3, In_2O_3 and Na_2CO_3 powders after pelletization and annealing in air [in the case of $NaIn(WO_4)_2$, at 1223 K for 50 h]. The production of bulk crystals is complicated by the fact that $NaIn(WO_4)_2$ melts incongruently at 1253 K, with the formation of solid $In_2(WO_4)_3$.[2,40–43]

A mechanochemical method calls for $NaIn(WO_4)_2$ to be formed according to reaction (1) immediately after MA [Figure 2(*a*)]. It can be seen that the MA product is greatly amorphized and lines of the initial reagents are also present (at the level of detector noise).

Let α to be determined as the degree of MA reaction (1). The weight of charge (1) after (H)-sampling was 13.108–1.29 = = 11.818 g. The recalculated initial weight (1.058 g) of Na_2CO_3 was 0.958 g. In this case, the calculated weight of removed CO_2 was 0.397 g. The weight loss of the drum after MA was 0.33 g. As a result, α(A) = 0.33 / 0.397 = 0.83.

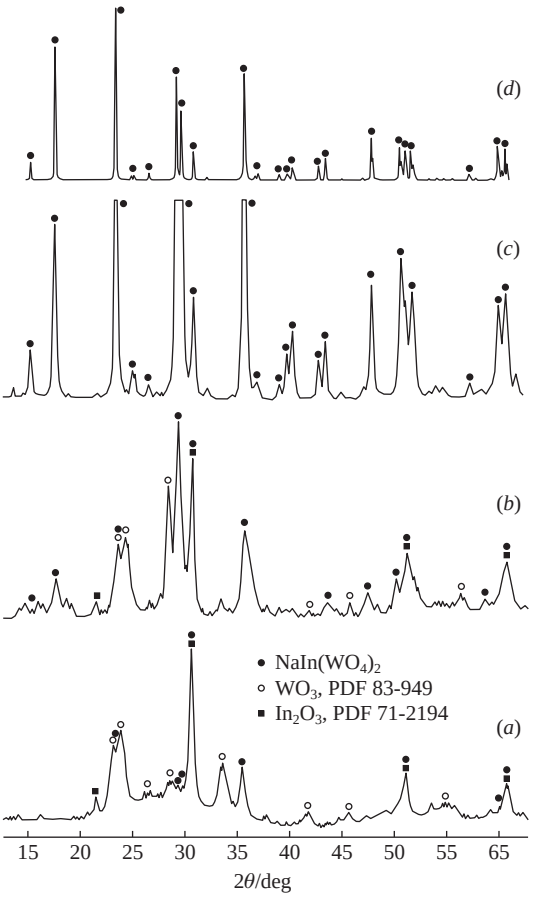


Figure 2 X-ray powder diffraction patterns for system (1): (*a*) MA product; (*d*) standard $NaIn(WO_4)_2$, PDF 74-2072, and see also synthesized $NaIn(WO_4)_2$ nanoparticles in ref. 44. MA product after annealing at (*b*) 773 K (500 °C) and (*c*) 973 K (700 °C).

Figures 2(*b*),(*c*) show the XRD data after the annealing of samples from the MA mixture (1). Annealing at 773 K [Figure 2(*b*)] leads to the partial crystallization of the MA product; however, the lines of starting reagents retained. As can be seen, pure $NaIn(WO_4)_2$ is produced at 973 K [Figure 2(*c*) is virtually identical to the standard in Figure 2(*d*)].

Hence, the MA method made it possible to lower the synthesis temperature of $NaIn(WO_4)_2$ from 1223 to 973 K and to shorten the synthesis time to 2 h. Note that the annealing of a MA sample at 973 K confirmed the above value α(A): α_{an}(A) = 0.84.

The DTA of MA mixture (1) showed the presence of at least one thermal effect at T = 698 K in addition to melting (Figure 3). The obtained melting point is 1273 K, which is consistent with published data[42] or 20 K higher.[1,40]

The preparation of nanocrystalline $NaIn(WO_4)_2$ by a modified Pechini sol–gel method with $D \approx 50$ nm at ~773 K was described.[44] Therefore, the thermal effect at 698 K can be attributed to crystallization with the formation of nanoscale $NaIn(WO_4)_2$ crystallites.

The dimensions of crystallites have been estimated by the Scherrer method based on an XRD reflection at 2θ = 35.65° [Figure 2(*b*)].[25,44] For the sample prepared as shown in the inset of Figure 3 (heating was stopped at 773 K), the value of D was 28 nm.

The use of very hard milling tools in mechanochemical reactors allows one to solve the problem of charge preparation for the growing of crystals. Since the abnormal,[45] autogenous[46] or semi-autogenous[47] wear of a milling tool material prevents a phenomenon involving self-lining (a layer of compact powder will be formed on the surface of milling tools) occurs.[33,48,49] For example, fine

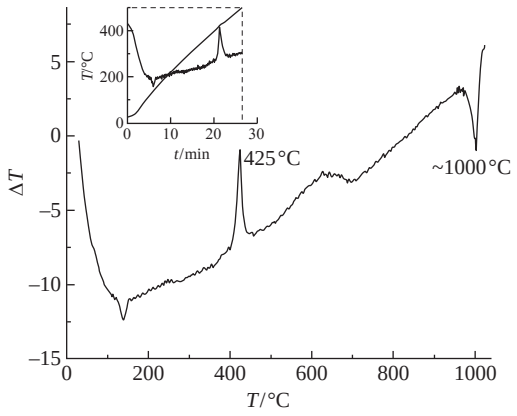


Figure 3 DTA pattern recorded for the MA sample system (1). Insert: a fragment of the DTA curve for the preparation of a special sample for XRD analysis.

crystal zirconia ceramic wear-resistant balls have the lowest self-wear rate in a fast-speed miller.[50] After annealing MA systems (2) at 973 K for 2 h, we produced a charge with a composition and structure suitable for growing the bulk crystal of $NaIn(WO_4)_2$ from MA system (1).[2]

Thus, according to thermal analysis data, the mechanical activation of the $Na_2O–In_2O_3–WO_3$ system resulted in the crystallization of $NaIn(WO_4)_2$ nanoparticles with sizes of about 30 nm at 698 K.

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