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Nanosized pure and Cr doped $Al_{2-x}In_x(WO_4)_3$ solid solutions

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ABSTRACT

For a first time are synthesized nanosized solid solutions with formula $Al_{2-x}In_xCr_y(WO_4)_2$ ($x = 0$–2, $y = 0.02$–0.1). Co-precipitation method is used for the synthesis. It is established that only by strict maintenance of pH between 2.7 and 2.9 a pure, monophase product of $In_2(WO_4)_3$ can be obtained. By X-ray powder diffraction and DTA/TG analyses, it is established that at room temperature the solid solutions $Al_{2-x}In_x(WO_4)_2$ at x value between 0 and 1.1 are orthorhombic and for x value between 1.1 and 2.0 are monoclinic. The phase transition temperatures are defined for different x values. Results from X-ray and TEM analyses show that nanosized pure $Al_{2-x}In_x(WO_4)_2$ and Cr-doped $Al_{2-x}In_xCr_y(WO_4)_2$ with size dimension between 10 and 40 nm can be successfully synthesized by co-precipitation method with subsequent thermal treatment at relatively low temperature (550 °C) for 1 h.

1. Introduction

Aluminium tungstate $Al_2(WO_4)_3$ and indium tungstate $In_2(WO_4)_3$ belong to a class of compounds with a general formula $Me_2(WO_4)_3$, where Me = Y, Sc, In, Al or lanthanides with a small ionic radius – Ho, Er, Tm, Yb, Lu. Normally, these compounds crystallize in an orthorhombic structure, space group Pnca [1]. As a result of phase transition, the structure transforms to monoclinic one at lower temperatures, space group P21/a. The phase transition of $In_2(WO_4)_3$ occurs at 250 °C [2], and of $Al_2(WO_4)_3$ occurs at −6 °C [3].

The tungstates of the lanthanides, $Ln_2(WO_4)_3$, Ln = Ho, Er, Tm, Yb, Lu, are hygroscopic, which restricts their potential applications as pure phases [4]. The specific features of orthorhombic structure, space group Pnca, determine a number of interesting properties and potential applications of the rest of the compounds.

The orthorhombic modification is built of MeO_6 octahedra, connected with WO4 tetrahedra in such a manner that they form a pseudo-layered structure with a large tunnel size, where the Me^{3+} ions are sufficiently mobile, that is, the compounds possess Me^{3+} ionic conductivity. The trivalent ionic conductivity of Al^{3+}, Sc^{3+}, Y^{3+} and Er^{3+} in the corresponding tungstates is directly demonstrated and described in reference literature [5–7]. The ionic conductivity in solid electrolytes depends not only on the ionic radius of the mobile Me^{3+} ion, but also on the available space for movement and the interaction forces between the ion and its adjacent ions, building the structure. Hence the increase of the lattice parameters with changes in the chemical composition would result in increase the ionic conductivity too. Similar behaviour has been already demonstrated by Sc_2-xLux$(WO_4)_3$ solid solutions, where the conductivity rises with the increase of lutetium [8]. The solid solutions of $(Al_2(WO_4)_3)_{1-x}(Sc_2(MoO_4)_3)_x$ are another example, where the conductivity is maximal for x = 0.6 [9]. As a result of investigations on the ionic conductivity in the system $Al_2(WO_4)_3$–$Sc_2(WO_4)_3$–$Lu_2(WO_4)_3$, a solid solution composition has been found with ionic conductivity, which is 25 times higher than that of $Al_2(WO_4)_3$ [10]. There are no data about the ionic conductivity of Al_{2-x} $In_x(WO_4)_3$ solid solutions.

Some of the $Me_2(WO_4)_3$ compounds possess unusually low thermal expansion coefficients, including zero and even negative ones, within a broad temperature range [11–14]. An important advantage of this class of compounds is their aptitude to build their structure by accumulation of different trivalent ions. This provides the possibility to tailor the thermal expansion coefficient to a desired value by varying the chemical composition of solid solutions with the mentioned structures. For example, a zero thermal expansion coefficient is reported for the $Al_{1.68}Sc_{0.02}In_{0.3}(WO_4)_3$ composition [15]. Such materials are very valuable for application in optics and optoelectronics. It is proved for Al_{2-x} $In_x(WO_4)_3$ solid solutions that the thermal expansion coefficient is slightly positive

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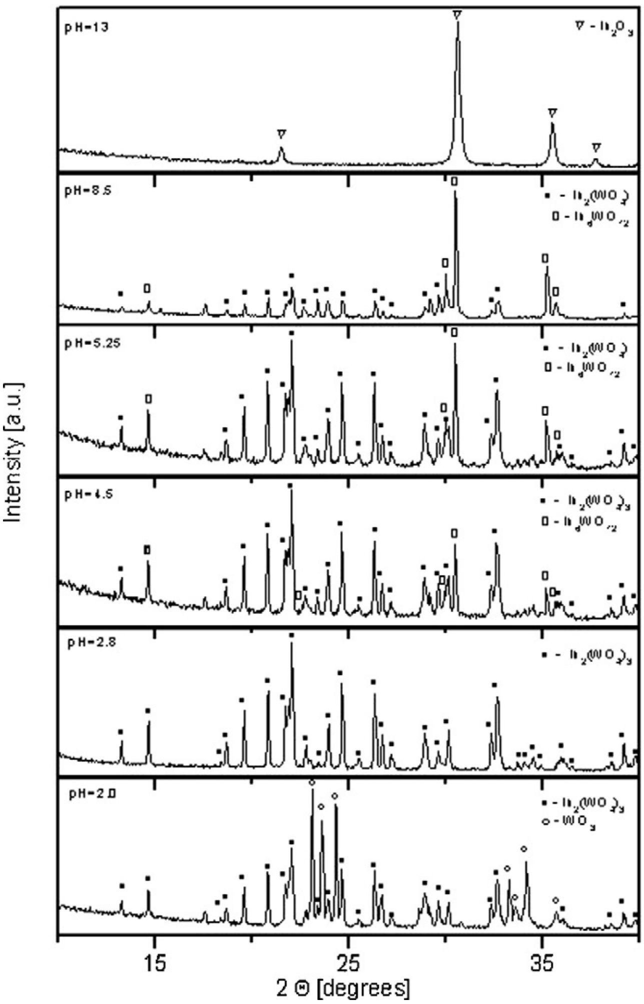

Fig. 1. X-ray patterns of precipitates obtained at different pH value and thermally treated at 900 °C for 3 h.

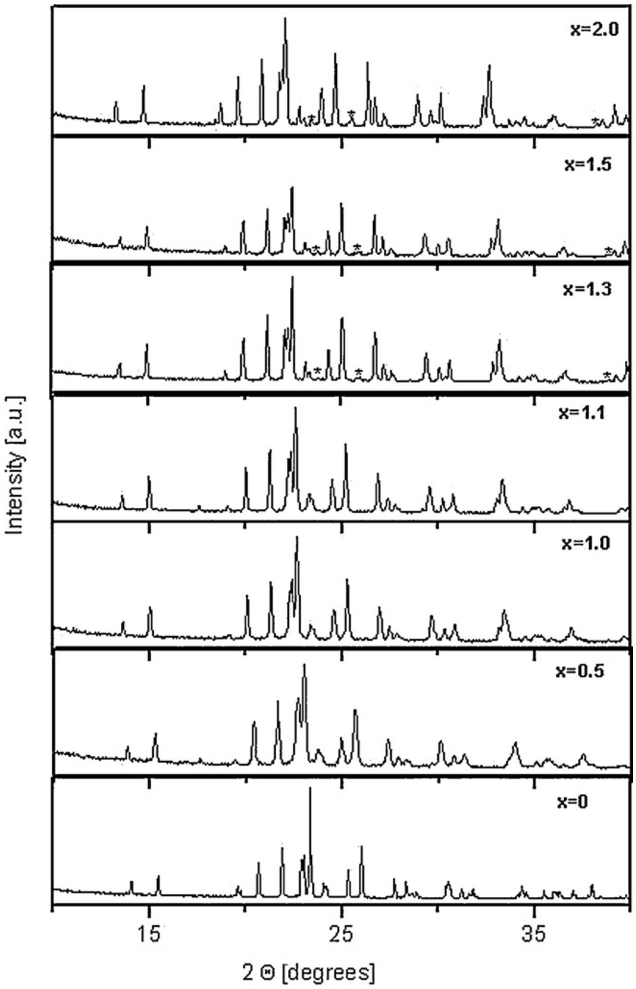

Fig. 3. X-ray patterns of the $Al_{2-x}In_x(WO_4)_3$ solid solutions with different x value, thermally treated at 900 °C for 3 h, * – marked picks corresponded to the monoclinic symmetry of space group P21/a.

and increases with the growth of In content for x value from 0.2 to 0.5. However, for $In_2(WO_4)_3$ the coefficient is negative at temperatures exceeding 250 °C (orthorhombic structure) and positive for temperatures lower than 250 °C (monoclinic structure) [15,16].

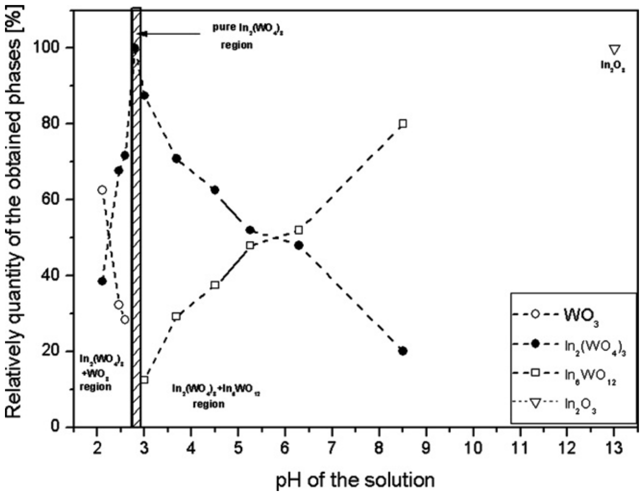

Fig. 2. Chemical composition of the obtained phases depending on the pH value of the solution after thermal treatment of the precipitates at 900 °C for 3 h.

Another basic application of this class of compounds is as laser media for tunable lasers. The Me^{3+} situated in octahedral coordination may be easily substituted by a Cr^{3+} active ion. This active ion is characterized by a broad absorption cross section, as well as by a broad emission, being incorporated in a structure with weak or medium strong crystal field, as it is in the case the $Me_2(WO_4)_3$ tungstates [17–19]. Our previous investigations on single crystal growth of $Al_{2-x}In_x(WO_4)_3$ solid solutions show that these solutions, doped with chromium, possess broad absorption cross section and medium strong crystal field [20,21].

The given brief review shows that the synthesis of tungstate solid solutions with different composition within the frames of the considered class of compounds represents an alternative to produce materials with optimal properties with respect to ionic conductivity, thermal expansion coefficient, as well as optical properties for laser active media.

Pure and chromium doped $Al_{2-x}In_x(WO_4)_3$ solid solutions are relatively insufficiently studies. This refers to the methods for their production (as a rule using only the classical solid state synthesis) and to already discussed applications.

Normally, the obtained classical solid state reaction products are chemically inhomogeneous, often containing admixture phases and relatively high level of pore. The study of the properties on the typical for the classical solid state synthesis products, often leads to unreliable results. In the opposite, the synthesis of nanosized powders by soft chemical methods provides compact, chemically