

## Growth and scintillation properties of NaLa(WO<sub>4</sub>)<sub>2</sub> and NaLa(MoO<sub>4</sub>)<sub>2</sub> single crystals

*V.N.Baumer, Yu.N.Gorobets, M.B.Kosmyna, B.P.Nazarenko,  
V.M.Puzikov, A.N.Shekhovtsov, O.V.Zelenskaya*

Institute for Single Crystals, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine,  
60 Lenin Ave., 61001 Kharkiv, Ukraine

*Received September 17, 2008*

Pure and doped NaLa(WO<sub>4</sub>)<sub>2</sub> and NaLa(MoO<sub>4</sub>)<sub>2</sub> single crystals have been grown by the Czochralski technique. The scintillation characteristics thereof have been determined and considered.

Методом Чохральского выращены чистые и активированные монокристаллы вольфрамата NaLa(WO<sub>4</sub>)<sub>2</sub> и молибдата NaLa(MoO<sub>4</sub>)<sub>2</sub>. Определены и проанализированы их сцинтилляционные характеристики.

Tungstate and molybdate single crystals of the scheelite structure type are widely used for various applications. For example, due to unique combination of high density  $\rho$ , high effective atom number  $Z_{eff}$  and fast scintillation response, the PbWO<sub>4</sub> crystals were used as the material for scintillation detectors of high energy physics projects [1]. In addition, Nd<sup>3+</sup> doped PbWO<sub>4</sub> crystals are active self SRS-conversion media of good promise [2]. The application areas of CaWO<sub>4</sub> and CdWO<sub>4</sub> crystals include the non-destructive control systems and medical diagnostics [3]. The presence of specific isotopes in tungstate crystals makes these materials suitable to study of rare nuclear reactions. In particular, <sup>100</sup>Mo and <sup>180</sup>W containing scintillation crystals are necessary for double beta-decay and alpha-decay investigations, respectively [4].

Therefore, to expand the series of scintillation crystals, of actual importance are further investigations of tungstate and molybdate crystal growth and their properties. The data on crystals growth and scintillation characteristics of pure and doped scheelite-like NaLa(WO<sub>4</sub>)<sub>2</sub> (NLWO) and NaLa(MoO<sub>4</sub>)<sub>2</sub> (NLMO) crystals containing

<sup>100</sup>Mo and <sup>180</sup>W isotopes have been first obtained in this work.

The charge for growth of pure and doped crystals was obtained by solid state synthesis. La<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> of special purity grade as well as WO<sub>3</sub> and MoO<sub>3</sub> of analytical reagent grade were used as the initial components. The stoichiometric composition blend was heated to 700°C for 5 h. X-ray phase analysis has shown a small amount of WO<sub>3</sub> phase in the NLWO blend. NLMO was free of impurity phases.

Because both crystals NLWO and NLMO are melting congruently at 1250°C and 1140°C, respectively, we used the Czochralski technique for crystal growth. The automated setup "Analog" equipped with weight control system was used to grow NLWO and NLMO crystals. The NLWO and NLMO crystals were grown on an oriented seed along [001] direction from 200 cm<sup>3</sup> Pt crucible. For NLWO crystals, we used nitrogen atmosphere, for NLMO, air. The crystal growth parameters were as follows: pulling rate 1–3 mm/h, rotation speed 20–30 min<sup>-1</sup>, temperature gradient 50–70 deg/cm. Impurities were introduced in the crystal as NaBi(WO<sub>4</sub>)<sub>2</sub>, Sb<sub>2</sub>O<sub>5</sub> and CuO compounds.

Table 1. Total concentrations of unintentional impurities in NaLa(WO<sub>4</sub>)<sub>2</sub> and NaLa(MoO<sub>4</sub>)<sub>2</sub> crystals

	Impurities, wt. %.					
	NaLa(MoO <sub>4</sub> ) <sub>2</sub>	Fe 7·10 <sup>-4</sup>	Cu 1·10 <sup>-4</sup>	Al 1·10 <sup>-4</sup>	Mg 1·10 <sup>-4</sup>	W 1·10 <sup>-3</sup>
NaLa(WO <sub>4</sub> ) <sub>2</sub>	Fe 6·10 <sup>-4</sup>	Cu 1·10 <sup>-4</sup>	Al 2·10 <sup>-4</sup>	Mg 2·10 <sup>-4</sup>	Mo 1·10 <sup>-3</sup>	Pb 3·10 <sup>-4</sup>

The crystal-melt interface was maintained to be flat or slightly convex. The crystal dimensions were as follows: length up to 60 mm, diameter up to 35 mm. All the crystals so grown were transparent and free of impurity phases and macroscale defects (gas bubbles, cracks, etc.). The total concentrations of unintentional impurities in NLWO and NLMO crystals are presented in Table 1.

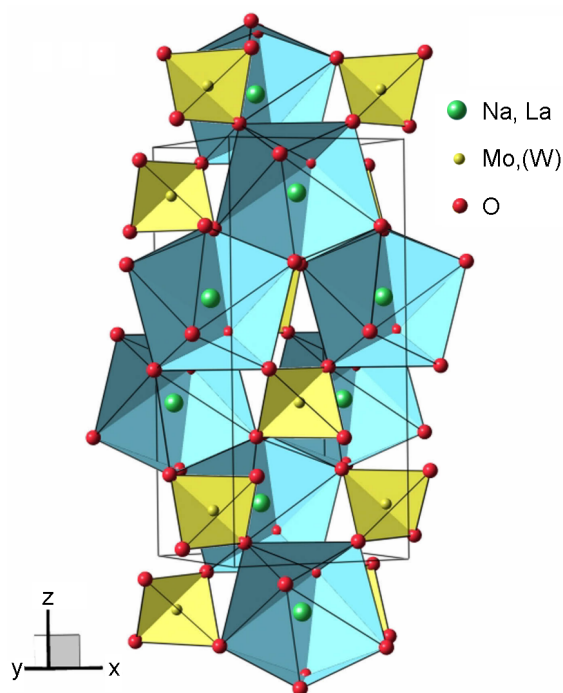
X-ray luminescence spectra were measured using an SDL-2setup. X-ray luminescence was excited by REIS-I X-ray sources ( $U = 30$  kV,  $I = 50$   $\mu$ A, Cu anticathode). The light yield (LY) was determined using a standard spectrophotometric setup consisting of a BUS2-94 preamplifier, a BUI-3K linear amplifier and an AMA-03-F multichannel pulse amplitude analyzer. A HAMAMATSU R1307 photomultiplier with 3 inch photocathode diameter was used as the photoreceiver. To excite the scintillations, a <sup>137</sup>Cs ( $E_\gamma = 662$  keV) radiation source was used. The light yield of the single crystals under study was normalized to the standard CsI(Tl) reference sample.

NLWO and NLMO crystals belong to the scheelite family, tetragonal system, space group  $I4_1/a$ . The structural base of NLWO and NLMO crystals consists of tridimensional skeleton. The skeleton formed by zig-zag-like chains of lanthanum and sodium polyhedrons (Fig. 1). La and Na are coordinated with eight oxygen atoms, tungstate (molybdenum), with four ones. La and Na polyhedrons are bonded together along lateral edges and form unlimited spirals around [001]. The peculiarity of this structure is statistical distribution of La and Na in the chains. The unit cell parameters are: for NLWO,  $a = 5.3544$   $\text{\AA}$ ,  $c = 11.6589$   $\text{\AA}$ ,  $Z = 4$ ; for NLMO,  $a = 5.3397$   $\text{\AA}$ ,  $c = 11.7294$   $\text{\AA}$ ,  $Z = 4$ .

Comparison of ionic radii of doping and matrix ions (Table 2) allows us to suppose most probable crystallographic positions of dopants. Because La<sup>3+</sup> and Na<sup>+</sup> are statistically distributed in the chains, we the same behavior of Cu<sup>+</sup> and Bi<sup>3+</sup> ions is to be expected. Cu<sup>+</sup> and Bi<sup>3+</sup> will substitute Na<sup>+</sup> and

Table 2. Ionic radii of matrix and doping ions

	Na <sup>+</sup>	La <sup>3+</sup>	Mo <sup>6+</sup>	W <sup>6+</sup>	Sb <sup>5+</sup>	Cu <sup>+</sup>	Bi <sup>3+</sup>
$R, \text{\AA}$	0.98	1.06	0.65	0.65	0.62	0.98	1.2

Fig. 1. Fragment of NaLa(WO<sub>4</sub>)<sub>2</sub> and NaLa(MoO<sub>4</sub>)<sub>2</sub> crystal structure.

La<sup>3+</sup> in the chains, respectively. Sb<sup>5+</sup> dopant will most likely occupy the crystallographic position of tungsten. The excessive negative charge may be compensated by oxygen vacancy.

According to [4], in tungstate and molybdate scheelite-like crystals, the conduction and valence bands are formed to a by electronic states of anionic complex (BO<sub>4</sub>)<sup>2-</sup> (where B = W and Mo) with different contributions of cationic states for different crystals. The luminescence spectrum of such crystals is characterized by the presence of several luminescent centers. One of those is connected with radiative transitions inside of (BO<sub>4</sub>)<sup>2-</sup> complex. The luminescence decay time of such centers is few nanoseconds. The other centers are con-

Table 3. Scintillation characteristics of NaLa(WO<sub>4</sub>)<sub>2</sub> and NaLa(MoO<sub>4</sub>)<sub>2</sub> crystals (∅20 mm, length 10 mm)

	$\lambda_{em}$ , nm	LY, photons/MeV	$\rho$ , g/cm <sup>3</sup>
NaLa(MoO <sub>4</sub> ) <sub>2</sub>	425	7	4.78
NaLa(Mo <sub>0.5</sub> W <sub>0.5</sub> O <sub>4</sub> ) <sub>2</sub>	420	5	5.66
NaLa(WO <sub>4</sub> ) <sub>2</sub>	435	8	6.53
NaLa(WO <sub>4</sub> ) <sub>2</sub> :Sb (0.5 wt.%)	435	11	6.53
NaLa(WO <sub>4</sub> ) <sub>2</sub> :Cu (0.5 wt.%)	475	8	6.53
NaLa(WO <sub>4</sub> ) <sub>2</sub> :Bi (0.5 wt.%)	480	8	6.53
NaLa(WO <sub>4</sub> ) <sub>2</sub> :Bi (2.5 wt.%)	480	7	6.53

nected with the presence of a defect (vacancy, impurity) near the regular (BO<sub>4</sub>)<sup>2-</sup> anionic group. The luminescence decay times of such centers vary within a wide range, from several microseconds to milliseconds. According to [5], two 4.2 ns and 1.2  $\mu$ s decay components were observed in NLMO crystals under X-ray quanta excitation. However, structures of optic centers in NLWO and NLMO crystals are unknown.

The long-wave fundamental absorption edges of NLWO and NLMO crystals are at  $\lambda = 320$  and  $370$  nm, respectively. Under excitation in those regions, both crystals demonstrate the similar luminescence spectra. The luminescence spectrum is broad and located in 350–600 nm range.

Scintillation characteristic measurement of NLWO, NLMO and NaLa(Mo<sub>0.5</sub>W<sub>0.5</sub>O<sub>4</sub>)<sub>2</sub> crystals has shown that light yield of all crystals is quite low (Table 3). The maximum light yield was observed for NLWO crystals, the minimum one, for NaLa(Mo<sub>0.5</sub>W<sub>0.5</sub>O<sub>4</sub>)<sub>2</sub>.

To improve the light yield, the attempts were made to increase the luminescent cen-

ter concentration in the NLWO crystal with the maximum light yield. To that end, Sb, Cu, and Bi were introduced into NLWO crystal. We supposed that these dopants will built in different sublattice of NLWO crystal and will create different structure luminescent centers. However, this did not improve the light yield considerably (Table 3).

### References

1. P.Lecoq, I.Dafinei, E.Auffray et al., *Nucl. Instrum. and Meth. Phys. Res. A*, **365**, 291 (1995).
2. T.T.Basiev, M.E.Doroshenko, L.I.Ivleva et al., *Kvant. Elektronika*, **36**, 720 (2006).
3. M.E.Globus, B.V.Grinyov, Inorganic Scintillators, Acta, Kharkov (2000) [in Russian].
4. A.N.Annenkov, O.A.Buzanov, F.A.Danevich et al., *Nucl. Instrum. and Meth. Phys. Res. A*, **584**, 334 (2008).
5. Y.Zhang, N.Z.Holzwarth, R.T.Williams et al., *Phys. Rev. B*, **57**, 12738 (1998).
6. S.B.Mikhrin, A.N.Mishin, A.S.Potapov et al., *Nucl. Instrum. and Meth. Phys. Res. A*, **486**, 295 (2002).

## Вирощування та сцинтиляційні характеристики монокристалів NaLa(WO<sub>4</sub>)<sub>2</sub> та NaLa(MoO<sub>4</sub>)<sub>2</sub>

**В.М.Баумер, Ю.Н.Горобець, М.Б.Космина, Б.П.Назаренко,  
В.М.Пузіков, О.Н.Шеховцов, О.В.Зеленська**

Методом Чохральського вирощено чисті та активовані монокристали подвійного вольфрамату NaLa(WO<sub>4</sub>)<sub>2</sub> та молібдату NaLa(MoO<sub>4</sub>)<sub>2</sub>. Визначено та проаналізовано їхні сцинтиляційні характеристики.