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Investigation of $CaMoO_4$ single crystals with low residual absorption☆

Nina S. Kozlova[a,*], Oleg A. Buzanov[b], Marina B. Bykova[a], Evgeniya V. Zabelina[a], Vasily N. Kornoukhov[c], Anna P. Kozlova[a], Anastasiia G. Chernykh[a]

[a] National University of Science and Technology "MISiS", 4 Leninskiy Prospekt, Moscow 119049, Russia
[b] Fomos-Materials OJSC, 16 Buzheninova Str., Moscow 107023, Russia
[c] Alikhanov Institute for Theoretical and Experimental Physics, 25 Bol'shaya Cheremushkinskaya Str., Moscow 117218, Russia

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ABSTRACT

Calcium molybdate enriched with the ^{100}Mo isotope ($^{40}Ca^{100}MoO_4$) is a promising material for use in cryogenic scintillation detectors. The main requirements of crystalline elements of the detector are absence of color and the attenuation coefficient (μ) not higher than 0.01 cm^{-1} at 520 nm wavelength. $^{40}Ca^{100}MoO_4$ and $^{40}Ca^{100}MoO_4$:Nb^{5+} single crystals have been investigated. The influence of isothermal annealing on the attenuation spectra in the 350 to 700 nm wavelength range has been studied. A broad absorption band with a maximum at λ=460 nm is observed in the attenuation spectra of the sample.

The dichroism phenomenon which is associated with anisotropy of the color centers in the crystals is observed along directions perpendicular to the optical axis. Annealing of the enriched samples at 1250 °C in an O_2 atmosphere leads to a substantial reduction of the intensity of the band near 460 nm.

The attenuation coefficient of the $^{40}Ca^{100}MoO_4$:Nb^{5+} crystals meets the requirement, which is $\mu \ll 0.01$ cm^{-1} at λ=520 nm. It is determined that absorption band near 460 nm and dichroism are absent.

Introduction

Calcium molybdate based crystalline materials show good potential for laser physics and acousto-optics due to a combination of a wide range of functional properties [1]. Currently these crystals are efficiently used as humidity sensors and optical elements of stimulated Raman scattering lasers.

Over the last decades there has been a growing interest toward $CaMoO_4$ (space group $4/m$, scheelite structure) because of its applicability as a material for cryogenic scintillation detectors [2,3]. Calcium molybdate crystals contain the ^{100}Mo molybdenum isotope for which the possibility of neutrinoless double beta-decay ($0\nu2\beta$) has been predicted, i.e. it can be used in the physics of elementary particles [4–6]. Authentic registration of neutrinoless double beta-decay could allow the scientists to determine the weight of the neutrino which is one of the most important tasks of advanced nuclear physics [7–9].

Efficient search for neutrinoless beta-decay requires a sensitive calcium molybdate functional elements with high optical and sufficient scintillation properties, and the contents of radioactive isotope impurities of the U-238 and Th-232 series should be at an unparalleled low level. The low-background plant should be installed deep underground with the aim of reducing the radiation background generated by space radiation and carefully screened with the use of radiation free materials [10,11].

In Russia, $^{40}Ca^{100}MoO_4$ single crystals for the functional elements of this type of detectors are only grown by Fomos-Materials OJSC. These crystals will be used by the AMoRE collaboration which works on the search for the neutrinoless double beta-decay of the ^{100}Mo isotope [10].

The radiation properties of crystal samples were studied at the Baksan Neutrino Observatory [11] and the YangYang Underground Laboratory, Korea, and the scintillation properties were studied at the Oxford University UK, and at the Physics Department of Tegu University in Korea [12]. The results showed that the quality of the crystals is insufficient for the stated objectives because $^{40}Ca^{100}MoO_4$ crystals grown in air acquire blue color.

The color of the crystals is caused by the color centers formed during the crystal growth [1]. This type of defects is generated in the crystals due to deviations of the melt composition from the stoichiometric one caused by high volatility of MoO_2 at above 650 °C.

Molybdenum in form of MoO_3 evaporates from the melt during the crystal growth, this process leads to the formation of molybdenum and oxygen vacancies $(V_{Mo})^{6-}$ and $(V_O)^{2+}$ [13]:

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* Corresponding author.
E-mail address: kozlova_nina@mail.ru (N.S. Kozlova).

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$CaMoO_4 \rightarrow CaMo_{1-y}O_{4-3y} + yMoO_3\uparrow$

Vacancy formation can be described as follows:

$Mo_{Mo}^{6+} + 3O_o^{2-} \rightleftarrows (V_{Mo})^{6-} + 3(V_o)^{2+} + MoO_3\uparrow$

If $^{40}Ca^{100}MoO_4$ single crystals are used in cryogenic scintillation detectors, crystal color in the working wavelength range 350–700 nm is quite undesired. Ttherefore decoloration is one of the most important tasks for the development of the production technologies of these crystals.

There are several options for the synthesis of $^{40}Ca^{100}MoO_4$ crystals with the required optical quality:

- doping with elements of valence 5, e.g. Nb^{5+} [1,14];
- addition of MoO_3 compensate the volatility of the components during the growth [15];
- optimization of oxidative annealing mode: varying process temperature, vapor pressure etc. [1,15].

The main requirement to the detector elements is that their attenuation coefficient (μ) is not higher than 0.01 cm^{-1} at 520 nm wavelength (maximum scintillation luminescence) [10]. Therefore it is crucial to study the attenuation spectra of the material as a function of growth conditions and subsequent treatment and to choose the optimum $^{40}Ca^{100}MoO_4$ crystal growth conditions, which provide the required material parameters.

Experimental

We studied calcium molybdate single crystals grown by Czochralsky method from high purity stoichiometric charge on Kristall-3M type plants in platinum crucibles with high-frequency heating. Figure 1 shows typical as-grown calcium molybdate crystals. The crystals have elliptical cross-sections of the cylindrical portion. The crystal sizes allow to fabricate cylindrical scintillation elements 40 mm in diameter and up to 50 mm in length. The optical parameters of the crystals were improved by various types of exposure during the growth as well as post-growth treatment.

The test specimens were cut from different crystals:

- as-grown $CaMoO_4$;
- $^{40}Ca^{100}MoO_4$ enriched with ^{100}Mo and ^{40}Ca and exposed to several stages of annealing in oxidizing atmosphere for extended time at 1250 °C;
- $^{40}Ca^{100}MoO_4$ doped with Nb^{5+} (0.024 wt%).

Figure 1. As-grown calcium molybdate single crystals.

We assessed the optical quality of single crystals by spectrophotometry on a Cary 5000 spectrophotometer in the optical range 350–700 nm in naturaly polarized light. This simple method is fast and non-destructive and allows to reveal the nature of defects and establish correlation between growth conditions and optical properties of the single crystals. This method is based on measuring the transmission coefficient $T(\lambda)$ in the working range 350–700 nm and calculation of the attenuation coefficient $\mu(\lambda)$ taking into account multiple internal reflections [16].

After measuring the transmission coefficient it is possible to calculate the attenuation coefficient using the following formula

$$\mu(\lambda) = -\frac{1}{d}\lg \tau_i(\lambda), \quad (1)$$

where d is the specimen thickness, cm, and $\tau_i(\lambda)$ is the spectral coefficient of internal transmission, rel. units.

The internal transmission coefficient $\tau_i(\lambda)$ at the wavelength λ is calculated using the formula

$$\tau_i(\lambda) = \sqrt{\left\{\frac{1}{T(\lambda)}\frac{8n^2(\lambda)}{[n(\lambda)-1]^4}\right\}^2 + \left[\frac{n(\lambda)+1}{n(\lambda)-1}\right]^4} - \frac{1}{T(\lambda)}\frac{8n^2(\lambda)}{[n(\lambda)-1]^4}, \quad (2)$$

where $T(\lambda)$ is the spectral transmission coefficient measured with a two-beam spectrophotometer of the Cary 5000 type, Rel. units and $n(\lambda)$ is the refraction coefficient of the specimen material for the respective wavelength λ.

We determined the refraction coefficients $n(\lambda)$ for the $CaMoO_4$ crystals based on earlier data [17].

To determine the attenuation coefficient $\mu(\lambda)$ according to [16], we compare the resultant internal transmission coefficient τ_i with 0.83. If $\tau_i(\lambda) < 0.83$ then the attenuation coefficient is calculated using Eq. (1), and if $\tau_i(\lambda) > 0.83$ then the following formula is used for calculation:

$$\mu(\lambda) = \frac{D(\lambda) - D_{\rho m}(\lambda)}{d}, \quad (3)$$

where d is the specimen thickness, cm, and $D(\lambda)$ is the optical density of the specimen calculated using the formula

$$D(\lambda) = -\lg \tau(l); \quad (4)$$

$D_{\rho m}(\lambda)$ is the correction factor, which takes into account radiation losses resulting from multiple reflections at both functional surfaces of the sample calculated as follows [16]:

$$D_{\rho m}(\lambda) = -\lg \frac{2n(\lambda)}{n^2(\lambda)+1}. \quad (5)$$

The error in the assessment of the attenuation coefficient is determined indirectly by taking into account the transmission coefficient measurement error and the sample thickness error. The attenuation coefficient measurement method accuracy does not exceed 2%.

Results and discussion

We investigated the effect of growth conditions and post-growth treatment of the crystals on attenuation spectra.

As-grown $CaMoO_4$. We studied the dispersion and anisotropy of the attenuation coefficient for $CaMoO_4$ cube shaped 10.9×10.9×10.9 mm^3 specimens. One of the cube surfaces was perpendicular to the optical axis (coincident with the Z axis in Figure 2). The specimens did not undergo any post-growth treatment. The $\mu(\lambda)$ measurement setup is shown in Figure 2. The results are presented in Figure 3.

The optical quality of the crystals should be assessed from the attenuation coefficient at 520 nm wavelength corresponding to the

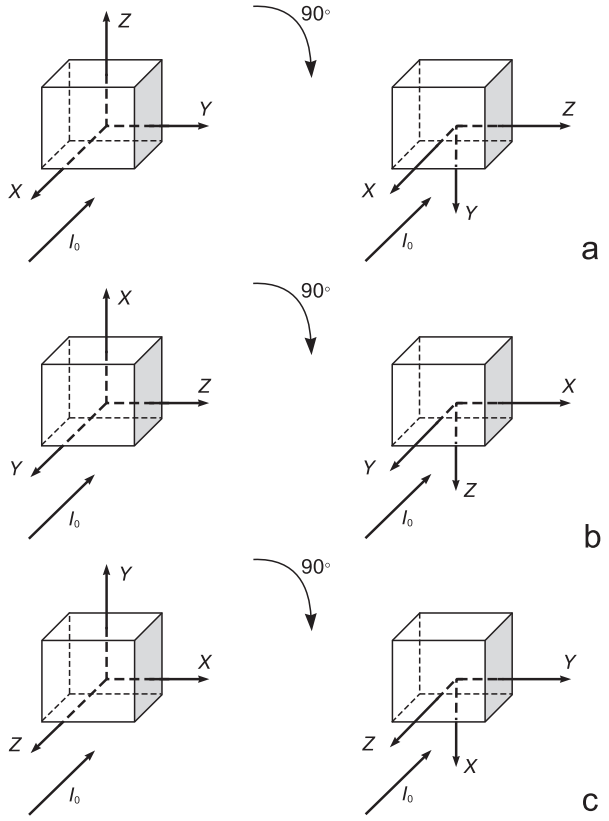

Figure 2. As-grown $CaMoO_4$ $\mu(\lambda)$ measurement setup: (a) measurements along the *X* and (*X*+90 arc deg) axes, (b) measurements along the *Y* and (*Y*+90 arc deg) axes and (c) measurements along the *Z* and (*Z*+90 arc deg) axes. *X*+90, *Y*+90 and *Z*+90 stand for 90 arc deg rotation about the *X*, *Y* and *Z* axes, respectively.

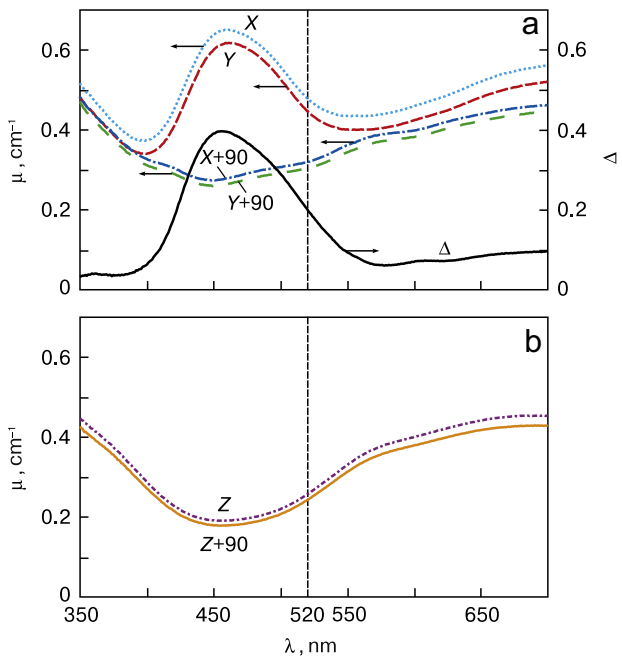

Figure 3. $\mu(\lambda)$ spectral for as-grown $CaMoO_4$ single crystals and dichroism degree Δ: (a) perpendicular to the optical axis and (b) along the optical axis.

maximum luminescence of calcium molybdate (see dashed lines in Figures 3–5). At this wavelength, these samples show $\mu > 0.01$ cm^{-1}.

All the spectra (Figure 3) contain a wide attenuation band with maximum at 460 nm. Analysis of the attenuation coefficient data along different coordination axes (*X* and *Y*) show a slight anisotropy. The

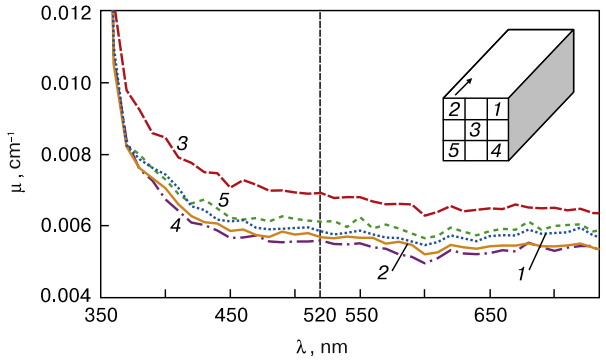

Figure 4. $^{40}Ca^{100}MoO_4$ specimen measurement setup and attenuation spectra for respective areas (*1–5*).

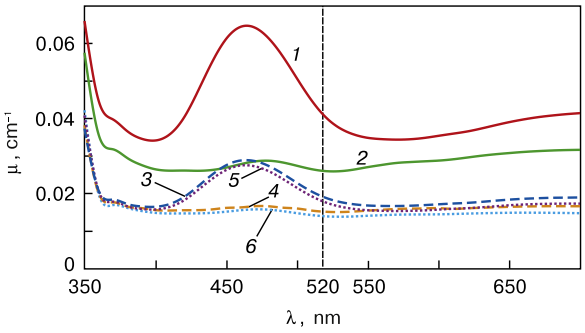

Figure 5. Attenuation spectrum for the central area of the $^{40}Ca^{100}MoO_4$ crystal along the *X* axis (*1*, *3* and *5*) and for *X*+90 arc deg) (*2*, *4* and *6*) after three test anneals: (*1* and *2*) first anneal, (*3* and *4*) second anneal and (*5* and *6*) third anneal.

scattering of the attenuation coefficient at λ~460 nm is approx. 4% depending on direction.

The dichroism phenomenon was observed near the band at 460 nm. This effect occurs when naturaly partially polarized light passes orthogonally to the optical axis of the crystal. When crystal is rotated by 90 degrees around beam incidence axis attenuation coefficient changes. It has been shown (Figure 3) that the attenuation coefficient at 460 nm is 0.65 cm^{-1} if viewed along the *X* axis and 0.29 cm^{-1} after sample rotation through 90 deg about the *X* axis; a similar effect is observed for the *Y* axis. No dischroism occurs for the *Z* axis. This indicates that color centers are anisotropic.

The degree of dichroism (*Δ*) was calculated using the following formula [18]:

$$\Delta = \frac{\mu_{max} - \mu_{min}}{\mu_{max} + \mu_{min}}, \quad (6)$$

where μ_{max} is the maximum attenuation coefficient for the experimental wavelength and μ_{min} is the minimum attenuation coefficient for that wavelength.

Figure 3a shows the Δ(λ) function. In the 400–660 nm range the pattern of the dischroism spectrum agrees well with that of the attenuation coefficient.

Effect of doping. As shown previously [1,14] doping of calcium molybdate crystals with an dopant substituting Mo^{6+} and having a lower valence reduces the intensity of blue color.

Therefore samples cut out from the Nb^{5+} doped $^{40}Ca^{100}MoO_4$ crystal were studied. We measured the attenuation coefficient in 5 different areas as per the measurement setup shown in Figure 4. The attenuation spectra (Figure 4) indicates a high optical quality of the crystal: the attenuation coefficient within the test region are was much lower than 0.01 cm^{-1} and no attenuation band typical of calcium molybdate in the 400–550 nm range is observed. Consequently, there is no dichroism.

Analysis of the spectra (Figure 4) shows that the sample has

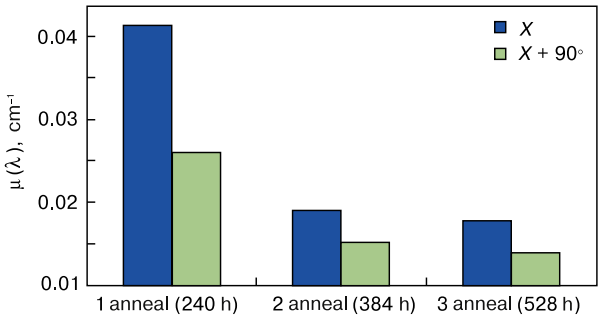

Figure 6. $^{40}Ca^{100}MoO_4$ crystal attenuation coefficient as a function of oxidative annealing duration (520 nm wavelength).

homogeneous distribution of the attenuation coefficient due to the fact that all the fluctuations are within the measurement method accuracy. In the central area (Figure 4, area 3) the attenuation coefficient is higher than in the other regions however it still meets the condition $\mu(\lambda) < 0.01$ cm^{-1}. This can be caused by an inhomogeneous impurity diffusion into the crystal or by growth defects.

Effect of annealing. As shown earlier [1,15] heat treatment in an oxidizing atmosphere can reduce the intensity of crystal color.

Therefore in order to reduce the concentration of color centers we exposed as-grown $^{40}Ca^{100}MoO_4$ crystals to isothermal annealing for different time at 1250 °C in a pure flow of O_2.

We made three test anneals and analyzed the crystals for attenuation coefficient homogeneity after each cycle. The attenuation spectra are shown in Figure 5. As there is no dichroism along the Z axis we only present the results for the X axis and for the 90 arc deg rotation about the X axis. Comparison of the attenuation spectra showed that $\mu(\lambda)$ decreases after each oxidizing anneal. At first the anneal of the $^{40}Ca^{100}MoO_4$ crystals at 1250 °C in an O_2 ambiance decolorizes the crystals and substantially reduces the attenuation band intensity and the degree of dichroism (Figure 5). After annealing for longer time the attenuation band intensity and the dichroism degree continue to decrease gradually, and saturate after annealing for 384 h or longer.

The μ level at 520 nm reached after annealing for a total of more than 520 h is still above 0.01 cm^{-1} (Figure 6).

Summary

We reported a spectrophotometric study of the attenuation spectra of $CaMoO_4$, $^{40}Ca^{100}MoO_4$ after isothermal annealing and doped $^{40}Ca^{100}MoO_4$:Nb^{5+} single crystals in the 350–700 nm range.

For the $CaMoO_4$ crystals the attenuation coefficient at 520 nm wavelength much higher than the level required for using these single crystals as materials for cryogenic scintillation detectors. The $\mu(\lambda)$ spectra contain a wide absorption band with maximum at λ=460 nm. If the light passes orthogonally to the crystal optical axis, dichroism occurs due to anisotropy of absorption centers. We calculated the degree of dichroism.

The results showed that oxidative annealing of the $^{40}Ca^{100}MoO_4$ crystals at 1250 °C in an O_2 atmosphere initially substantially reduces the 460 nm absorption band intensity and the attenuation. However, the required attenuation was not achieved regardless the long total annealing time (> 520 h).

The attenuation coefficient of the Nb^{5+} doped calcium molybdate single crystals meets the above requirements and is $\mu(520\text{ nm}) \ll 0.01$ cm^{-1}. Furthermore, the spectrum of this specimen does not contain the band at 460 nm and no dichroism occurs.

During the preparation of this manuscript we optimized the growth technology and the heat treatment parameters according to the above stated results. Study of the crystals grown using the optimized technique shows that optical parameters are close to the existing standard requirements.

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