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Research Article

Effect of post-growth anneals in oxygen-containing atmosphere on the microhardness of single crystal calcium molybdate $CaMoO_4$

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Abstract

Single crystal calcium molybdate $CaMoO_4$ is a well-known material. However the interest to $CaMoO_4$ has recently grown due to a number of its important applications including as a working material in cryogenic scintillation bolometers. $CaMoO_4$ single crystals acquire blue color during growth due to the presence of color-center type defect centers which are unacceptable for optical applications. Color can be eliminated through annealing in an oxygen containing atmosphere, following which required optical components can be produced from the single crystals by mechanical treatment (cutting, polishing etc.). Therefore assessment of the mechanical properties of these single crystal materials is an important task for the optimal solution of issues occurring in the fabrication of optical components and their further practical application. There are but scarce data on the mechanical properties of $CaMoO_4$, and the available ones have been reported without allowance for anisotropy. There is a significant scatter of data on the Mohs hardness of the single crystals, ranging from 3.3 to 6 in different publications. In this work we present data on calcium molybdate single crystals in the initial state and after high-temperature anneals of different durations in an oxygen containing atmosphere. We show that long-term annealing leads to decolorization of the crystals. Calcium molybdate single crystals prove to be quite brittle: the brittleness index *Zp* of the crystals in the initial state is the highest and equals 5, while annealing reduces the brittleness index to 4. The Palmqvist toughness factors *S* have been calculated The limit indentation destruction loads F_{lim} have been determined and annealing in an oxygen containing atmosphere has been shown to increase F_{lim} by 2.5 times for the *Z* cut and by 10 times for the *X* cut. The microhardness of the crystals has been shown to exhibit a II type anisotropy: the microhardness of all the specimens was higher for the *Z* cut than for the *X* cut. The microhardness anisotropy coefficients *KH* of the specimens have been evaluated. The bond ionicity degree *I* has been calculated on the basis of the experimentally measured microhardness.

Keywords

single crystals, uniaxial single crystals, calcium molybdate, annealing in an oxygen containing atmosphere, mechanical properties, microhardness, Vickers hardness, anisotropy coefficient, brittleness, bond ionicity

1. Introduction

Synthetic calcium molybdate (powellite) $CaMoO_4$ is a well-known material. The first works dealing with this material date back to the 1940s [1]. Calcium molybdate $CaMoO_4$ single crystals have a scheelite type structure, tetragonal system, space group $I4_1/a$, point group $4/m$. The unit cell of calcium molybdate is tetragonal body centered, containing 4 formula units. For a scheelite structure the $[MoO_4]^{2-}$ anion tetrahedrons are interconnected by Ca^{2+} ions surrounded by eight oxygen ions and form zigzag-shaped chains. The bonds between the Ca^{2+} cations and the $[MoO_4]^{2-}$ anion are ionic, while those between molybdenum and oxygen in the $[MoO_4]^{2-}$ anion are covalent [2–4]. There is a large scatter between literary data on the *a* and *c* lattice parameters of the calcium molybdate crystals (Table 1).

Table 1. $CaMoO_4$ crystal lattice parameters

#	Lattice parameter (nm)		Source
	a	*c*	
1	5.213	11.395	[2]
2	5.222	11.425	[5]
3	5.226	11.430	[6]
4	5.349	12.020	[3]

Single crystal calcium molybdate was initially used in tunable acousto-optic filters [2, 7, 8], and later on in Raman lasers [9]. The growth of interest to this material in recent years has been caused by the possibility of using isotope-enriched calcium molybdate $^{40}Ca^{100}MoO_4$ in the search for neutrinoless double beta decay as a working component of the cryogenic scintillation bolometer cell [10–12]. Practical applications of these crystals in optics are limited by the presence of color-center type defect centers showing themselves in the form of yellow, blue or bright-blue color [2, 12–14]. This color of the crystals is typically attributed to the presence of oxygen vacancies after oxygen release in the form of volatile molybdenum oxide MoO_3 during growth [2]. Isothermal anneals in an atmosphere containing a controlled amount of oxygen lead to decolorization of these crystals [2, 13, 14].

Along with the requirement to transparency in the working wavelength range and other requirements, calcium molybdate crystals are also expected to exhibit appropriate mechanical properties [2]. Correct knowledge of the mechanical properties of commercial crystals is critical for the optimal solution of device operation issues. In practice, mechanical properties are sensitive for mechanical treatment [2] since the hardness and brittleness of the crystals dictates crystal handling practices avoiding cracks or scratches caused by mechanical impacts during crystal holding, moving and clamping. The hardness and brittleness of the material are the first parameters to be determined. The hardness of the crystals is controlled by crystallochemical parameters such as crystalline structure type, valence of constituent elements, unit cell parameters and types of chemical bonds; hardness is sensitive to the chemical composition and anisotropic [15–17].

Hardness is defined as crystal's resistance to cutting, scratching or indentation. The numerical unit of hardness is the ratio between the indentation load and the dimensions of the indentation produced by the indenter, or the width or length of the scratch produced on the crystal's face [17]. If the indentation load is less than 2*N* (~203.94 g) and the indentation depth is more than 20 nm, it is said that microhardness is dealt with [18]. For rough estimation of hardness, Mohs' decimal scale is used (Mohs Hardness, HM): if a mineral can scratch a reference mineral, its hardness is higher in the Mohs scale, otherwise if a mineral is scratched by a reference mineral, its hardness is lower [18].

Anisotropic media to which calcium molybdate refers may exhibit I and II type hardness anisotropy. I type anisotropy is polar anisotropy which depends on indenter axis direction relative to the crystallographic directions of the crystal face, whereas II type anisotropy implies different microhardness for different crystal faces [20].

Calcium molybdare microhardness data are quite scarce in literature and are presented without allowance for anisotropy or specification of indentation loads applied. Furthermore, the data available have a noticeable scatter (Table 2).

The aim of this work is to study the effect of isothermal anneals in an oxygen containing atmosphere on the microhardness of $CaMoO_4$ single crystals and its anisotropy.

2. Experimental

The $CaMoO_4$ crystals were grown at FOMOS-Materials JSC with the Czochralsky technique from stoichiometric charge with an addition of an excess of MoO_3 in Pt crucibles on a Kristall-3M growth set up with RF heating. The crystals were cut into oriented 10 × 10 × 10 mm dice with the *Z* (001) faces perpendicular to the 4th order axis.

The specimens were studied as-grown and as-annealed for different time (6 and 1000 h) in an oxygen containing

Table 2. $CaMoO_4$ hardness data

Year	Plane	Mohs Hardness	Source
1950	Not Specified	3.5	[21]
2001–2005	Not Specified	3.5–4	[5]
2008	Not Specified	4	[2]
1988	(011)	5.3	[22]
	(001)	4.8	
2002	Not Specified	6	[23]

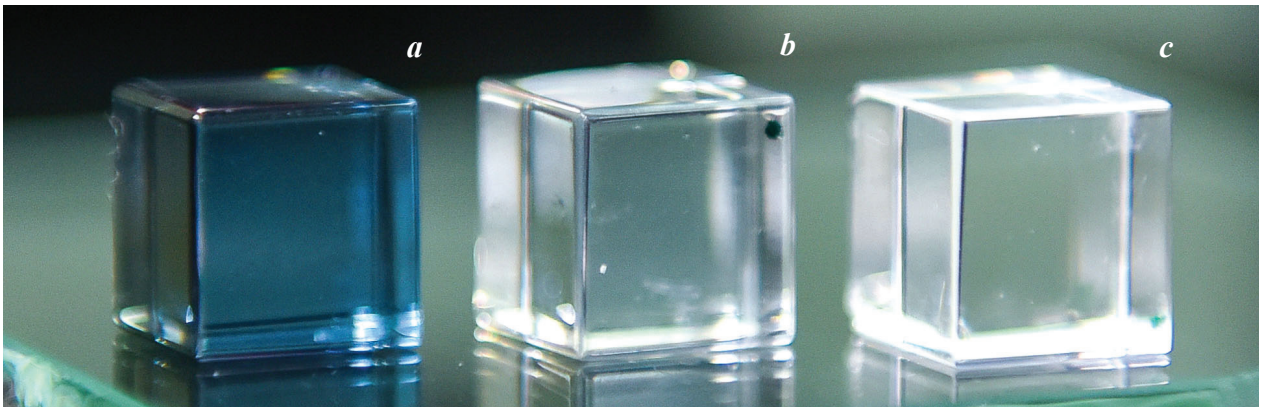

Figure 1. Calcium molybdate crystal specimens: (*a*) initial deep blue, (*b*) light-blue annealed for 6 h and (*c*) colorless annealed for 1000 h

atmosphere at T = 1000 °C. The unannealed specimens (initial state) were deep blue in color, those annealed for 6 h were light-blue in appearance and those annealed for 1000 h were colorless. Photos of the specimens are shown in Fig. 1.

In this work, the hardness was tested by the Vickers method (Vickers Hardness, HV) [16, 18, 24–26]. Vickers diamond probe is used in this method as the indenter, its shape being a regular four-faceted diamond pyramid with a square base and the angle α = 136 arc deg between opposite faces at the pyramid vertex. Vickers hardness data are taken after the removal of the indentation load, so the effect of elastic strain generated by the indenter impact is not allowed for.

The Vickers hardness is proportional to the indentation load divided by the indentation base surface area, the latter being calculated from the lengths of its diagonals in the assumption that the indentation has a regular pyramid shape with a square base and the vertex angle equal to the indenter's vertex angle, and is calculated using the following equation [16, 18, 24–26]:

$$\mathrm{HV} = \frac{1}{g_n}\frac{2F\sin\frac{136^\circ}{2}}{d^2} \approx 0.1891\frac{F}{d^2}, \quad (1)$$

where F is the load, N, g_n is the gravitational acceleration, a is the angle between opposite faces at the pyramid vertex equaling α = 136 arc deg, and d is the arithmetic mean of the indentation diagonals d_1 and d_2 after indentation load removal, mm.

The microhardness was measured at the Inter-University Test Laboratory for semiconductors and dielectrics "Single Crystals and Stock on their Base" on a calibrated Aaffri DM 8 B microhardness meter allowing indentation testing at small loads, beginning from 1 g. The dwell time was 10 s, the load rate being 30 mm/s. The microhardness was calculated automatically from the measurements of the indentation diagonals using a CCD camera with the Hardtest-Program Precidure Ver. 2.4 software of Frits Mueller GmbH. HV measurement correctness was controlled directly before specimen testing by measuring the hardness of the lithium fluoride (LiF) reference specimen produced and tested at the Inter-University Test Lab. The measurement accuracy was not worse than 5%.

3. Results

All the specimen surfaces were indented using the same method taking into account crystal orientation (Fig. 2).

The measurements were carried out at 1, 3, 5, 10 and 25 g loads.

For a 1 g load the indentations were irresolvable regardless of specimen type. For a 3 g load the indentations were surrounded by cleaves and cracks for all the specimens regardless of crystal face orientation. This observation suggests that the $CaMoO_4$ crystals are extremely brittle.

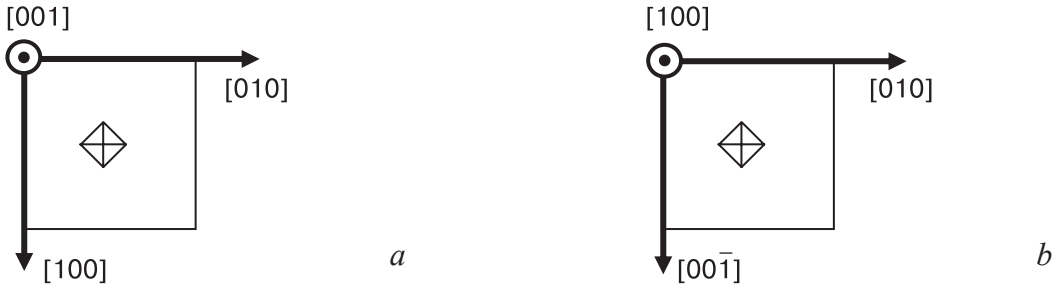

Figure 2. Schematic of indentations on (*a*) *Z* and (*b*) *X* crystal faces

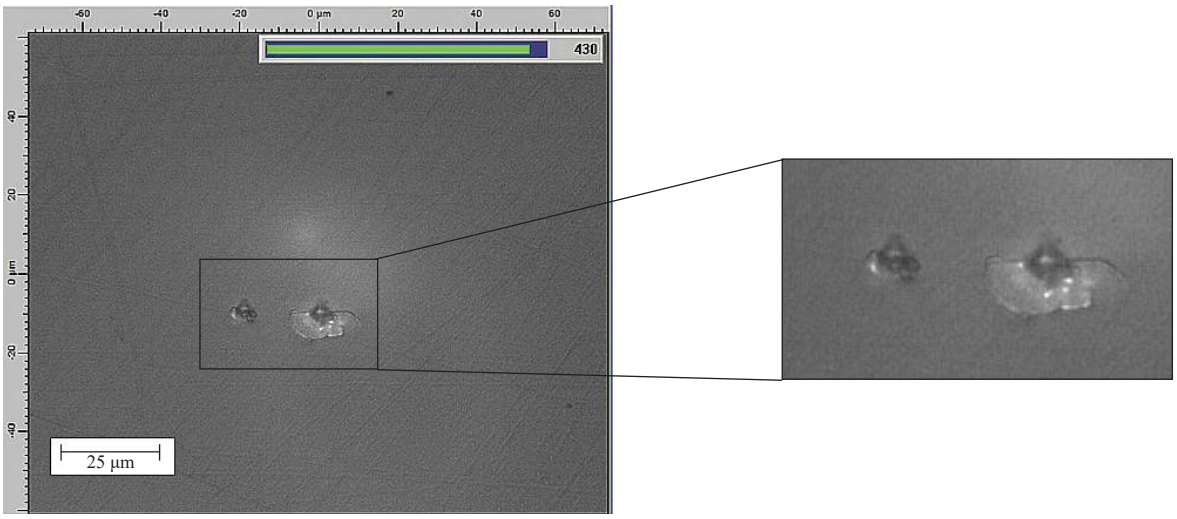

Figure 3. Typical indentations on the *Z* cut of the light-blue specimen (loads 5 and 10 g, respectively)

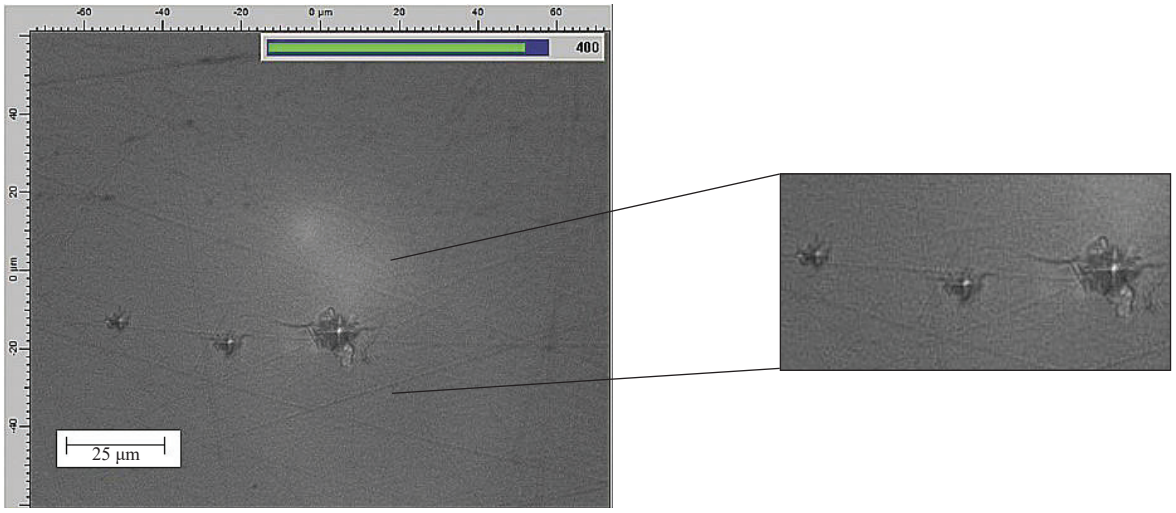

Figure 4. Typical indentations on the *X* cut of the colorless specimen (loads 5, 10 and 25 g, respectively)

Typical calcium molybdate microhardness indentations are shown in Figs. 3 and 4.

For understanding the complete indentation destruction evolution the indentation load was increased to the limit indentation destruction load F_{lim}. The following F_{lim} were obtained for the test specimens:

– 10 g for the *Z* cut and 5 g for the *X* cut of the initial specimen;

– 25 g regardless of face orientation for the light-blue specimen annealed for 6 h;

– 25 g for the *Z* cut and 50 g for the *X* cut of the specimen annealed for 1000 h.

Isothermal oxygen annealing increased F_{lim} by 2.5 times for the *Z* cut and by 10 times for the *X* cut.

The as-annealed specimens were less brittle than the as-grown ones. The high brittleness of materials us

Table 3. Material brittleness evaluation [27]

Average brittleness index	Indentation pattern
0	Indentation without visible cracks or cleaves
1	One minor crack at indentation corner
2	One crack not aligned with indentation diagonal. Two cracks at adjacent indentation corners
3	Two cracks at opposite indentation corners. Three cracks at different indentation corners. Cleave at one indentation side
4	More than three cracks. Cleaves at two indentation sides
5	Complete destruction of indentation shape

typically attributed to the fact that the load exerted by the diamond pyramid during indentation exceeds the limit strength of the material [27] resulting in the material having insufficient ability to disperse elastic stress and hence specimen destruction. Thus annealing of the crystals in an oxygen containing atmosphere increases the limit strength of $CaMoO_4$.

For numerical evaluation of the material's brittleness, the brittleness index *Zp* and the Palmqvist toughness factor *S* were calculated [27].

The brittleness index of the specimens was evaluated using the method described earlier [27] according to which each indentation is assigned a brittleness index in an arbitrary 5-points scale [27] (Table 3) taking into account the number of cracks and cleaves in the vicinity of the indentations and their propagation patterns.

The average brittleness index of the $CaMoO_4$ specimens as determined in accordance with the abovementioned approach [27] and Table 3 is 4–5.

Palmqvist toughness factor evaluation [27] implies measuring the work (toughness) *S* performed by the force (load) F_{cr} during indentation, with only those loads being taken into account at which 50% of indentations have cracks. If the indenter is a diamond pyramid with a square base and a 136 arc deg vertex angle, the ductility factor is calculated using the following formula:

$$S = 2\sqrt{\frac{F_{cr}^3}{HV}}. \quad (2)$$

Since cracks occurred at each of the indentations, the ductility was calculated for all the loads used.

For the specimens whose microhardness could be measured for different loads, an increase in the microhardness either remains the same within the experimental error with a change in the ductility (*Z* cut, annealed for 1000 h) or increases with an increase in the ductility (*Z* cut, initial and annealed for 6 h; *X* cut, annealed for 1000 h).

Vacuum annealing increases the ductility of all the test specimens regardless of cut orientation.

The resultant HV microhardness was converted to Mohs hardness HM since in the literary available publications [2, 5, 21–23] the microhardness of calcium molybdate was represented in the Mohs scale. The conversion formula was as follows [27]:

$$HM = 0.675\sqrt[3]{HV}. \quad (3)$$

The microhardness data are close to the earlier literary ones [22, 23] but differ from those presented in other publications [2, 5, 21]. The microhardness for a 5 g load is the highest for the initial blue specimen and the lowest for the 6-h annealed light-blue specimen. The microhardness of the colorless specimen annealed for 1000 h is intermediate between the above two figures.

All the test specimens exhibited II type microhardness anisotropy: the microhardness of the *Z* faces was higher than that of the *X* ones. The microhardness anisotropy is the greatest for the unannealed blue specimen and the smallest for the annealed colorless one. The difference of the microhardness between different crystal faces is caused by the difference in the structures, primarily the reticular density (number of lattice sites per unit area) and the bond strength between the lattice sites [15]. The reticular density of $CaMoO_4$ single crystals is higher for the *Z* faces than that for the *X* faces which is in a good agreement with the microhardness data for these faces.

The anisotropy coefficient KH is used to evaluate the anisotropy degree for anisotropic materials, its formula being as follows [16]:

$$KH = \frac{H_{max}}{H_{min}}, \quad (4)$$

where H_{max} is the highest microhardness and H_{min} is the lowest microhardness.

Due to the brittleness of the crystals the microhardness anisotropy coefficient was determined in accordance with Eq. (4) for different loads and yielded as follows:

– 1.064 for the initial blue specimen (load 3 g);

– 1.061 for the annealed light-blue specimen (load 10 g);

– 1.02 for the annealed colorless specimen (load 25 g).

Microhardness measurements allow evaluating the bond ionicity degree in accordance with the following earlier formula [28, 29]:

$$HM = mI^2 + kI + l, \quad (5)$$

where *I* is the bond ionicity degree and *m, k* and *l* are constants.

The closer the resultant *I* to 1 the greater the bond ionicity degree of the material in question. The highest hardness is observed in crystals with a substantially greater covalent bond component as compared to those having predominantly ionic bonds [27]. The ionic (or covalent) bond type is characteristic of the symmetry of the electron bonds localized between the atoms.

It was shown [28, 29] that the constants $m = 15.79$, $k = 11.33$ and $l = 7.63$ are suitable for a wide range of materials. Thus taking into account these values the following final formula was used in this work for bond ionicity degree evaluation:

$$I = \frac{-11.33 - \sqrt{11.33^2 + 4 \cdot 15.79(7.63 - HM)}}{-2 \cdot 15.79}. \quad (6)$$

The bond ionicity degree calculated using Eq. (6) for the test crystals proved to be higher for the *Z* faces than for the *X* ones. Furthermore the lower the bond ionicity the higher the microhardness, in agreement with earlier data [27].

The HV and HM microhardness data, the bond ionicity degree *I*, the hardness anisotropy coefficient KH, the brittleness index *Zp*, the Palmqvist toughness factor *S* and the limit indentation destruction load F_{lim} for the $CaMoO_4$

Table 4. Parameters of $CaMoO_4$ specimens taking into account anisotropy in the initial state and after isothermal anneals in an oxygen containing atmosphere

Parameter		Specimen						
		Initial		Light-blue, annealed for 6 h		Colorless, annealed for 1000 h		
Load		3 g	5 g	5 g	10 g	5 g	10 g	25 g
Z cut	HV, kgf/mm^2	410±20	460±20	340±20	450±20	390±20	380±20	–
	HM	5.0	5.2	4.7	5.2	4.9	4.9	–
	I	0.90	0.89	0.92	0.89	0.91	0.91	–
	F_{lim}, gf (mN)	10 (98.07)		25 (245.2)		25 (245.2)		
	S, kgf/mm	0.52	1.04	1.21	2.98	1.13	3.26	–
X cut	HV, kgf/mm^2	350±20	–	–	380±20	–	360±20	410±20
	HM	4.7	–	–	4.9	–	4.8	5.0
	I	0.92	–	–	0.91	–	0.91	0.90
	F_{lim}, gf (mN)	5 (49.03)		25 (245.2)		50 (490.3)		
	S, kgf/mm	0.56	–	–	3.26	–	3.34	12,30
KH		1.064	–	–	1.061	–	–	1.021
Zp		5		4		4		

specimens obtained in this work are summarized in Table 4 taking into account the anisotropy and annealing time.

4. Conclusion

First $CaMoO_4$ microhardness data were obtained for specimens in the initial as-grown state and after high-temperature anneals in an oxygen containing atmosphere. $CaMoO_4$ specimens are quite brittle, cracks and cleaves occurring in the vicinity of indentations at such a small load as 3 g for all the test specimens. Limit indentation destruction loads F_{lim} were determined taking into account the anisotropy and specimen annealing time. Isothermal annealing in an oxygen atmosphere increases the limit indentation destruction load by 2.5 times for the *Z* cuts and by 10 times for the *X* cuts of the specimens.

Crystal brittleness was characterized with brittleness indices *Zp* and Palmqvist toughness factors *S*. Annealed specimens are less brittle than unannealed ones.

The experimental Mohs microhardness figures HM are ~5 for the *Z* cut and ~4.7 for the *X* cut in the initial state. The specimens were found to exhibit II type microhardness anisotropy, the microhardness for the *Z* cuts being higher than that for the *X* cuts of all the test specimens. The anisotropy coefficient KH was determined.

Based on the microhardness data the bond ionicity degree was determined for the $CaMoO_4$ specimens in the initial state and after isothermal anneals in an oxygen containing atmosphere.

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