Nd Pronounced Anharmonicity in IR Spectra of CaWO₄ Single Crystals

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Abstract:
CaWO₄ and Nd:CaWO₄ (0.8 at. % Nd) single crystals were grown from the melt by the Czochralski technique in air. The crystal growth parameters \( d_c \) and \( \omega_c \) were calculated by equations from the hydrodynamics of the melt, whereas the rate of crystal growth was experimentally obtained. The infrared reflectance spectra of Nd:CaWO₄ and CaWO₄ single crystals were recorded in the range 50-5000 cm\(^{-1}\) at room and liquid nitrogen temperatures. Two oxygen \( E_u \) modes showed a splitting. That especially concerns one of them where the splitting is even more pronounced with the Nd doping. Instead of the earlier attempts based on a symmetry breaking or an activation of forbidden modes, we suggest that a strong anharmonicity is the source of this effect.

Keywords: Crystal growth; X-ray diffraction; IR spectra; Anharmonicity.

Introduction

Calcium tungstate (CaWO₄) belongs to a group of AWO₄ compounds, where A is a metallic ion in the second group of the periodic table. Scheelite-type AWO₄ binary oxides are important materials due to their use as scintillator detectors, photoanodes, solid laser hosts, and in optical fiber applications [1, 2]. Calcium tungstate is a uniaxial crystal with the tetragonal scheelite structure and space group C\(_{4h}\), and has been proved an efficient laser host material with a number of doped lanthanide ions [3]. The trivalent lanthanide ions are known to occupy the divalent calcium ion site, with the S\(_4\) point symmetry, making the host lattice as an interesting system to study. The scheelite structure [3] may be regarded as a cubic close-packed array of Ca\(^{2+}\) and [WO₄]\(^{2-}\) units with the coordination numbers of 8 and 4 oxygen atoms for the Ca and W cations, respectively.

Various techniques such as the Czochralski technique [4, 5], flux method [6, 7], and solid-state reactions [8] have been used to synthesize single crystals, whiskers, and powder of CaWO₄. Some attempts were made on the preparation of single crystal films [9-11], but these experiments had limited success because of the high vaporization pressure of WO₃ and obtained films did not have a uniform structure. In our previous paper [4, 5], we obtained CaWO₄ and Nd:CaWO₄ single crystals using the Czochralski technique taking hydrodynamics equations into account, as we have successfully done for many oxide single crystals [12-15]. The aim of the present paper was to reveal and explain the observed

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peculiarities and the Nd induced changes in the infrared spectra of high quality CaWO₄ and Nd:CaWO₄ single crystals. The Nd content was 0.8 at. %, as is usual for laser materials.

Experimental

Pure and neodymium doped calcium tungstate single crystals (CaWO₄ and Nd:CaWO₄) were grown in air by the Czochralski technique using a MSR 2 crystal puller, as described previously [4, 5]. The rhodium crucible (4.12 cm ≥ 3.6 cm and 0.2 cm thick) was placed into an alumina vessel surrounded by ZrO₂ wool isolation. Double walls were used for a protection against the high radiation. To decrease the radial temperature gradient in the melt, alumina surrounded the system. The pull rate was in the range 0.54-12 mm/h, and the best results were obtained for both materials at the pulling rate of 6.7 mm/h. The crystal rotation rate was evaluated using the hydrodynamics equations, and the critical value was 30 rpm in both cases. The critical diameter of CaWO₄ and Nd:CaWO₄ crystals were found to be 1 cm. The crucible was not rotated during growth. After the growth run, the crystal boule was cooled down to room temperature at the rate of about 50 K/h.

The chemical composition was determined by XRD on powders. A Phillips 1710 diffractometer with a radiation λCuKα₁ = 0.15405 nm source and original APD software were used. The samples were pressed into standard aluminium frames and the measured range for 2θ was from 10° to 80°. The spectra were obtained at the step of 0.02°. For production identification, the MPDS program and JCPDS (ASTM) card files were used.

The infrared spectra were recorded on a Bomem DA8 Fourier-transform spectrometer. A wide-range hyper splitter was used for the far infrared region (from 20-700 cm⁻¹) and a standard KBr (400-5000 cm⁻¹) one for the mid infrared region. All the spectra were recorded at a near normal incidence for two different temperatures (T = 80 K, and 298 K). The measurements were performed using a Janis STDA 100 cryostat, which enabled precise exchange of the sample and the mirror at the same spot on the cold finger. At lower temperatures, a polyethylene (far IR) and ZnSe (mid IR) window were used. As a coolant, liquid nitrogen (LN₂) was used.

Results and discussion

When single crystals are grown by the Czochralski technique, two types of convection are usually observed in the melt, the buoyancy driven convection flow due to temperature gradient in the bulk melt and the centrifugal force driven by the rotation of the crystal [16]. These convection types are usually described by dimensionless numbers and these measures are, for the driving forces by crystal rotation, the Reynolds number (Re) and, for buoyancy, the Grashof number (Gr). It was presumed, as Carruthers [17] suggested, that there was no change in kinematic viscosity at the melt/crystal interface during the growth process and there was equilibrium Gr=Re². There is, this time, a flat interface melt/crystal with critical rotation rate ωc and critical diameter dc. We decided to use the relations derived by Carruthers in calculations for our experimental system. The crucible is considered to be stationary, during the crystal rotation at the constant rate. Tangential stresses generated by surface tension gradients are applied to account for Marangoni flow (described by the dimensionless Ma number), while no flow is allowed normal to the melt meniscus. Conduction and convection caused pulling are included in the crystal and rod pull rod. To simplify the current analysis, it was decided to neglect the effects of internal radiation through the crystal. The Ma number does not change significantly if a small temperature gradient exists over the surface of the melt, and so the hydrodynamics will be governed mainly by the Re and Gr numbers. The structure of CaWO₄ is presented in Fig. 1.
The unit cells of CaWO$_4$ and Nd:CaWO$_4$ were calculated by the least square method using 29 reflections including more K$_{\alpha 2}$ for 8 reflections. All the reflections corresponded to a CaWO$_4$ crystal with parameters of a tetragonal unit cell with $a = 0.524294$ (6) nm and $c = 1.1373$ (7) nm [4]. Our calculated results for the lattice parameters are $a = 0.5206$ (6) nm, $c =$
1.1363 (5) nm for CaWO$_4$ [4], and \(a = 0.52464 \ (6)\), \(c = 1.1362 \ (6)\) for Nd:CaWO$_4$ [5], which are in good agreement with the published data [18]. An X-ray diffractogram for powdered Nd:CaWO$_4$ is given in Fig. 2, where the Nd:CaWO$_4$ plate is shown in the inset.

The optical spectra of Nd:CaWO$_4$ and CaWO$_4$ single crystals were recorded in mid IR and far IR region at room temperature (298 K) and at liquid nitrogen temperature (80 K). The reflectance spectra of both single crystals are similar in the range 50-1100 cm$^{-1}$, the peak positions are almost at the same place. The reflectance spectra of Nd:CaWO$_4$ and CaWO$_4$ single crystals at both temperatures are shown in Fig. 3.

![Fig. 3](image)

**Fig. 3** Reflectance spectra of Ca$_{0.92}$Nd$_{0.08}$WO$_4$ and CaWO$_4$ single crystals in the range 50-1100 cm$^{-1}$ at T=80 K and T=298 K for the \(E \perp c\) polarization.

CaWO$_4$ is a crystal of the scheelite type, having \(C_{4h}\) point group and \(I4_1 / a\) space-group, with two formula units per primitive cell [19]. The Ca and W ions are at \(S_h\) sites, whereas the oxygen ions are at \(C_1\) sites. Factor group analysis in the \(C_{4h}^6 - I4_1 / a\) space group gives the following set of irreducible representations that characterize all the vibration modes for a tetragonal scheelite primitive cell \((k=0)\):

\[
\Gamma_{\text{tot}} = 3A_g + 5B_g + 5E_g + 5A_u + 3B_u + 5E_u. \quad (1)
\]

Among these, \(3A_g + 5B_g + 5E_g\) are the Raman-active modes and all species \(E\) vibrations are doubly degenerate [20]. After subtracting two \(A_u + E_u\) acoustic and \(3B_u\) forbidden modes, only 8 infrared–active modes remain:

\[
\Gamma_{\text{IR}} = 4A_u + 4E_u. \quad (2)
\]

The polarization \(E \perp c\) corresponds to \(E_u\) modes. Due to a weak coupling between the \([WO_4]^2-\) cluster and the \(Ca^{2+}\) ion (see Fig. 1) it might be a good approximation to label vibrations as internal or external, where “internal” refers to motion in which the center of
mass of the WO$_4^{2-}$ ion does not move, and “external” refers to motion of [WO$_4^{2-}$] ions as rigid units. In our case 2E$_u$ internal vibrations of the tetrahedral [WO$_4^{2-}$] ion are the high frequency oxygen modes at 306 and 796 cm$^{-1}$ (TO modes of Nd:CaWO$_4$ at 80 K) as in Figure 3. In contrast to low energy external E$_g$ modes, both of these lines show a splitting in our spectra and it is even more pronounced in Nd:CaWO$_4$. Barker [21] did not observe the splitting but still added some extra weak oscillators in order to improve the fit. According to his opinion such modes could arise from a selection rule breakdown or from a multiphonon absorption (combination bands). He offered a possible explanation for the polarization E $\perp \epsilon$, while the polarization E $\parallel \epsilon$ remained unexplained. First we consider the symmetry reasons of the observed splitting. The physical insight is granted by further labeling the internal modes as if each of them is designated having the [WO$_4^{2-}$] ion as a free molecule. The T$_d$ symmetry of a free tetrahedral [WO$_4^{2-}$] ion is reduced to S$_4$ in the crystal lattice [22, 23]. The presence of two WO$_4$ groups in each primitive cell further alters the symmetry to C$_{4h}$. These symmetry changes remove the degeneracy of the vibrational wave functions, which characterizes free [WO$_4^{2-}$] ions. We do not see any ground for a possible symmetry rule breaking or any departure from a pure scheelite structure which was additionally confirmed by our XRD measurements. In addition, 0.8 at. % Nd$^{3+}$ cannot change the lattice symmetry substantially.

It is very interesting that an exceptional splitting of the 306 cm$^{-1}$ mode appeared in both samples, where the Nd dopant additionally intensifies this effect. Nd$^{3+}$ ion exchanges the Ca$^{2+}$ one in CaWO$_4$. It is also worth emphasizing that Nd ions have a much larger ionic radius than Ca ions. CaWO$_4$ is a highly ionic crystal with a partly involved covalent bond. From the cationic point of view, the scheelite structure of CaWO$_4$ consists of two intercalated diamond lattices: one for Ca cations and another for W cations as in Fig. 1, where the Ca-Ca distances are equal to W-W distances. Calcium (Ca) cations are coordinated by oxygen (O) anions thus forming CaO$_8$ polyhedral units. On the other hand, tungsten (W) cations are coordinated by four O anions forming relatively isolated WO$_4$ tetrahedral units [24]. In the cation coordination notation for CaWO$_4$ compounds, scheelites have cation coordination [8–4].

In literature[25], it was found that the internal mode at 306 cm$^{-1}$ has part of a 92% O-W-O bond, 6% Ca-O bond, 1% O-Ca-O bond and 1% W-O-Ca bond, while the other at 796 cm$^{-1}$ has a 97% W-O bond and 3% Ca-O bond. It is obvious that the behaviour of these modes must be different, while the explanation about the influence of Nd ions still remains unclear as the Ca-O bond exist in both models. Some authors [26] tried to explain the splitting at 796 cm$^{-1}$ using Davidov splitting proposing that the symmetry of the [WO$_4^{2-}$] anion is broken and the intermolecular valence vibration $v_3$ ($F_2$) is split in E and B symmetry, while the mode at 306 cm$^{-1}$ is not taken into account since it is far away from the observed mode and its deformation vibrations could be a cause for this splitting. This is not in accordance with factor group analysis and this explanation was rejected as incorrect.

In order to explain the earlier mentioned discrepancy between the number of E$_g$ infrared-active modes from the factor-group analysis and the observed number of modes in the infrared spectra, we propose that anharmonicity could play a crucial role. The crystal structure has been described as highly ionic, with Ca$^{2+}$ cations and tetrahedral [WO$_4^{2-}$] anions, where the [WO$_4^{2-}$] anions are themselves highly ionic [22]. A peculiar temperature dependence of the observed 306 cm$^{-1}$ mode points to a strong anharmonic effect. Namely, the intensity ratio of the modes at 205 and 306 cm$^{-1}$ depends strongly on temperature as shown in Fig. 3. The enhanced splitting at 306 cm$^{-1}$ in Ca$_{0.92}$Nd$_{0.08}$WO$_4$ compared to the host material can be assigned to a large ionic radius of Nd$^{3+}$. Namely, even a small concentration of a large ion exchanging Ca$^{2+}$ in a strong ionic bond could cause pronounced anharmonicity. Therefore, we apply the standard factorized four-parameter model [27] of the dielectric function involving anharmonic effects:

$$\varepsilon(\omega) = \varepsilon_\infty \prod_j \frac{\omega_j^{2\mu\omega} - \omega_j^{2\omega} - 2\omega_j^{\mu\omega} \cdot \sum_{\mu\omega} (\omega, T)}{\omega_j^{2\omega} - \omega_j^{2\mu\omega} - 2\omega_j^{\mu\omega} \cdot \sum_{\mu\omega} (\omega, T)}$$

(3)
Where $\Sigma_{j\,TO(LO)}(\omega, T)$ is the self energy of the TO and LO mode, respectively:

$$\Sigma_{j\,TO(LO)}(\omega, T) = \Delta \omega_{j\,TO(LO)}(\omega, T) - i \Gamma_{j\,TO(LO)}(\omega, T)$$

(4)

If an intense two-phonon peak exists at the frequency $\omega_{2\,TO(LO)}$ due to an anharmonic interaction, a simplified relation holds [28]:

$$\Sigma_{j\,TO(LO)}(\omega, T) = \Delta \omega_{j\,TO(LO)}^2(T) - i \Gamma_{j\,TO(LO)}^2(T) + \frac{g_{j\,TO(LO)}^2(T)}{\omega - \omega_{2\,TO(LO)}(T) + i \Gamma_{j\,TO(LO)}^2(T)}$$

(5)

In our case, we observed a strong anharmonicity just for TO(3) and TO(4) modes at 306 and 796 cm$^{-1}$, which gives equation (3) in the following form:

$$\epsilon(\omega) = \epsilon_\infty \prod_{j=1}^{\infty} \left( \frac{\omega_{j\,LO}^2 - \omega^2 - i \omega_{j\,LO} \Gamma_{j\,LO}}{\omega_{j\,TO}^2 - \omega^2 - i \omega_{j\,TO} \Gamma_{j\,TO}} \right) \prod_{j=1}^{4} \left( \frac{\omega_{j\,LO}^2 - \omega^2 - i \omega_{j\,LO} \Gamma_{j\,LO}}{\omega_{j\,TO}^2 - \omega^2 - 2 \omega_{j\,TO} \Gamma_{j\,TO} + \Sigma_{j\,LO}(\omega, T)} \right)$$

(6)

Fig. 4. The fitted spectra of Ca$_{0.92}$Nd$_{0.08}$WO$_4$ single crystal in the range 50-1100 cm$^{-1}$ at T=80 K for the E $\perp$ c polarization. The modes at 306 and 796 cm$^{-1}$ were fitted taking into account the anharmonic effects (solid line). The dotted curve denotes the fit without an anharmonic correction whereas the asterisks correspond to experimental data.

Based on the above relations, we fitted the spectrum of Nd:CaWO$_4$ at 80 K. Fig. 4 shows the fitted spectra of a Nd:CaWO$_4$ single crystal. The fitted parameters are presented in Tab. I.
Tab. I  Fitted parameters of No: CaWO₄ spectra

| Phonons | ε∞ | ωTO | ωLO | ΓTO | ΓLO | g' | ΓTO 0 | ΓTO a | ΔωTO |
|---------|----|-----|-----|-----|-----|----|-------|-------|-------|
| 1       | 3.4| 143.5| 152.5| 3.7 | 3.7 | 4  | 4     | 4     | 4     |
| 2       |    | 204  | 252  | 5.7 | 5.7 | 4  | 4     | 4     | 4     |
| 3       |    | 366  | 8.7  | 8.7 | 323.5| 4.5| 4     | 10.3  | 1.5   |
| 4       |    | 903  | 8.5  | 839 | 24  | 7  | 17    | 1.5   |       |

In Fig. 4 the distinction between the anharmonic (solid line) and the harmonic fit (dotted line) is clearly seen.

Conclusion

The conditions for growing CaWO₄ and Nd:CaWO₄ single crystals were calculated using a combination of Reynolds and Grashof numbers. From the hydrodynamics of the melt, the critical crystal diameter dₓ = 1.0 cm and the critical rate of rotation ωₓ = 30 rpm were obtained. The value of the crystal growth rate was experimentally found to be 6.7 mm/h.

The Eₓ modes at 306 and 796 cm⁻¹ showed a strong splitting in the IR spectra. The splitting of the 306 cm⁻¹ phonon is even pronounced with Nd doping. Instead of the earlier attempts based on a symmetry breaking or forbidden modes, we suggest that a strong anharmonicity is the source of this effect.

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References

1. A. Kuzmin, J. Purans, Rad. Measur. 33 (2001) 583
2. A. A. Kaminskii, H. J. Eichler, K. I. Ueda, N. V. Klassen, B. S. Redkin, L. E. Li, J. Findeisen, D. Jaque, José Garcia-Sole, J. Fernández, R. Balda, Appl. Opt. 38 (1999) 4533
3. E. Guermen, E. Daniels, J. S. King, J. Chem. Phys. 55 (1971) 1093
4. A. Golubović, S. Nikolić, S. Đurić, A. Valčić, Metalurgija 9 (2003) 121 (in Serbian)
5. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, J. Serb. Chem. Soc. 68 (2003) 1001
6. S. Oishi, M. Hirao, J. Mater. Sci. Lett. 8 (1989) 1397
7. S. Oishi, M. Hirao, Bull. Chem. Soc. Jpn. 63 (1990) 984
8. G. Blasse, L.H. Brixner, Chem. Phys. Lett. 173 (1990) 409
9. C. Feldman, J. Soc. Motion Pict. Eng. 67 (1958) 455
10. W.S. Cho, M. Yashima, M. Kakihana, A. Kudo, T. Sakata, M. Yoshimura, Appl. Phys. Lett. 66 (1995) 1027
11. N. Saito, A. Kudo, T. Sakata, Bull. Chem. Soc. Jpn. 69 (1996) 1241
12. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, J. Serb. Chem. Soc. 64 (1999) 553
13. A. Golubović, S. Nikolić, R. Gajić, S. Đurić, A. Valčić, Hem. Ind. 53 (1999) 227 (in Serbian)
Садржај: Монокристали CaWO₄ и Nd:CaWO₄ (0.8 % am. Nd) су расли из растопа на ваздуху по методи Чохралског. Параметри раста кристала из растопа dₐ и ωₐ су израчунати помоћу једначина динамике флуида, док је брзина раста кристала добијена експериментално. Рефлексиони спектри монокристала Nd:CaWO₄ и CaWO₄ су снимани на собној температури и температури течног азота у опсегу таласних бројева 50-5000 cm⁻¹. Два E₂ мода кисеоника су показала раздвајање. То је посебно изражено на оном моду чије је раздвајање чак појачано допирањем са Nd. Уместо ранјих покушаја заснованих на поремећају симетрије или активирању забрањених модова, ми, на основу добијених резултата, предлажемо да је јака енхармоничност узрок тог ефекта.

Кључне речи: Раст кристала; дифракција Х-зрака; Инфрацрвени спектри; Енхармоничност.