

Vibrational Raman and FTIR Studies of Some Double Alkali Molybdates/Tungstates*

Usha Saraf and P. K. Bajpai

Department of Pure and Applied Physics
Guru Ghasidas Vishwavidyalaya, Bilaspur 495009 (C.G.) India
E-mail: bajpai.pk1@gmail.com

R. N. P. Chowdhury

Department of Physics and Meteorology
Indian Institute of Technology, Kharagpur (W.B.), India

(Received December 21, 2009)

Abstract: In this paper, we present the analysis of room temperature IR and Raman spectra of CsLiMoO₄/ CsLiWO₄ stabilize in cubic structural form. The expected vibrational modes in infrared and Raman spectra are estimated using factor group analysis and assignment of observed modes is attempted based on FGA predictions, reported assignments of internal modes of MoO₄/WO₄ in various compounds and splitting of degenerate internal modes. The results are discussed in terms of their effect on electronic band structure. Infrared and Raman spectra of polycrystalline alkali metal double molybdates CsLiMoO₄/ CsLiWO₄ were measured in the range 40-1000 cm⁻¹ at room temperature. To determine the symmetries and nature of the observed modes a factor group analysis has been performed. The crystal structure of the compounds studied depends on the type of cation and changes from trigonal to monoclinic and triclinic (for the lithium and sodium derivatives). The assignment of the observed bands to the respective internal and external vibrational modes is proposed.

Keywords: Infra-red spectra, Raman spectra, vibrational symmetry, group theoretical analysis

1. Introduction

Molybdates and tungstates are promising materials due to their high ionic and electron conductivity, luminescence, ferroelectric, piezoelectric and catalytic properties¹. The transition metal oxides of molybdates/tungstates with d₀ configuration belong to the most stable class of materials used as photo anodes. They find wide applications as scintillation detectors, laser host materials and in optical fibers. Transition metal tungstates /

*Presented at CONIAPS XI, University of Allahabad, Feb. 20-22, 2010.

molybdates have been studied widely due to their use as laser host and display materials. However, the tungstates / molybdates of alkali metals are rarely explored. Aleksandrov et al² studied the double alkali tungstates CsLiWO₄ (CLM) and molybdates CsLiMoO₄ (CLM) and RbLiMoO₄ (RLM) in their ferroelectric phase. These belong to cubic eccentric space group T_d²/F43m and show remarkable piezoelectric effect and second optic harmonic generation³⁻⁵. Their structure is based on a frame of corner linked MoO₄ and LiO₄ tetrahedra and topologically related to high cristobalite form of SiO₂. The cristobalite form is shown in figure 1. Cristobalite has an isometric structure, in which six-membered rings of (SiO₄)⁻⁴ tetrahedra are stacked parallel to (111). This arrangement of tetrahedra is analogous to the stacking of spheres in cubic closest packing. The large disorder produced due to variation of alkali ionic size gives interesting properties and variety of structural phases in these materials. It is also interesting to note that indirect band-band transitions in transition metal molybdates / tungstates are assisted by internal vibrations of tetrahedral ion. Therefore any distortion created at local level could be utilized for application by manipulating the band energy gap. Thus, the vibrational studies become very important, especially in double alkali molybdates / tungstates, for which such vibrational studies are sporadic only.

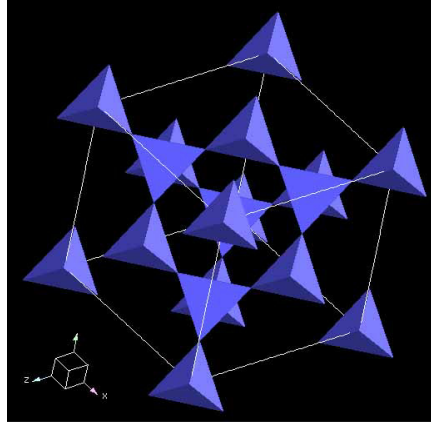
2. Phonon modes in CsLiWO₄/CsLiMoO₄: Factor Group Analysis

The expected vibrational modes in infrared and Raman spectra are estimated using factor group analysis and assignment of observed modes is attempted based on FGA predictions, reported assignments of internal modes of MoO₄/WO₄ in various compounds and splitting of degenerate internal modes. CsLiMoO₄ undergoes a series of phase transitions from high temperature cubic phase (Space group F43m/Td²) to trigonal phase at 211 K (Space group R3m/C_{3v}⁵) which transforms into monoclinic phase (Bm/C_{3s}) at 177 K. the Number of formula units in unit cell Z=4, 3 & 2 respectively in cubic/trigonal and monoclinic phase. Crystal exhibits ferroelectricity below 221K². Similar structural transition sequence is also reported in CsLiWO₄ with T_{c1} (from cubic to trigonal phase) at 221K and T_{c2} (from trigonal to monoclinic phase) at 191K. The number of formula units is also same in each phase as that in CLM. The unit cell parameters and density is shown in Table 1.

The crystal structure is based on a frame of corner linked MoO₄ and LiO₄ tetrahedral and is topologically related to the high cristobalite form of SiO₂ as shown in Figure 1.

Table 1: Phase sequence and Unit cell parameters in CsLiMoO₄/CsLiWO₄

CsLiWO₄	Phase III Monoclinic	Phase II Trigonal	Phase I Cubic	Transition temperature (T _c)
State	Ferroelectric Z=2	Ferroelectric Z=3	Paraelectric Z=4	I→II T _{c1} = 221K II→III T _{c2} = 191K
Space group	Bm-C _s ³	R3m-C _{3v} ⁵	F43m-T _d ²	
Unit cell Parameters	a=5.85Å; b=5.86Å c=10.25Å □ □ =125.5°	a=5.91Å; □=59.5°	a=8.350Å	
CsLiMoO₄	Phase III Monoclinic	Phase II Trigonal	Phase I Cubic	Transition temperature (T _c)
State	Ferroelectric Z=2	Ferroelectric Z=3	Paraelectric Z=4	I→II T _{c1} = 211K II→III T _{c2} = 177K
Space group	Bm-C _s ³	R3m-C _{3v} ⁵	F43m-T _d ²	
Unit cell Parameters	a=5.84Å; b=5.86Å c=10.21Å □ □ =125° .30'	a=5.89Å; □=59° .29'	a=8.318Å	

Figure .1: Cristobalite structure of SiO₂; CLM and CLW stabilize in the same form.

Large alkali cation occupy one half of the 12 coordinated laves polyhedral of frame. The Wyckoff position are Li⁺ (4c), Cs⁺ (4b), Mo²⁺ (4a) and O²⁻ (3bi). The former three have (43m/Ta) site symmetry, whereas 9bi has C₁ symmetry. At room temperature, four cations of each types in unit cell occupy the T_d sites, where as 16 O²⁻ occupy C₁ sites. The numbers of atoms that remain invariant under various symmetry operation of factor group are shown in table 2.

Table 2: Number of invariant atoms in each symmetry operation of Td group in CsLiMoO₄/CsLiWO₄

Symmetry element $\rightarrow$ T_d^2 -Space group	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$N_R(\text{Li})$	4	4	4	4	4
$R_R(\text{Cs})$	4	4	4	4	4
$N_R(\text{Mo})$	4	4	4	4	4
$N_R(\text{O})$	16	0	0	0	0
$N_R(\text{CsLiMo/WO}_4)$	28	12	12	12	12

The factor group analysis results are given in table 3.

Table 3: Results of Factor Group Analysis for $\text{CsLiMoO}_4/\text{CsLiWO}_4$

Φ	0	120	180	90	0
$\cos \Phi$	1	-0.5	-1	0	1
$2 \cos \Phi \pm 1$	3	0	-1	-1	1
$\chi_R(\text{Li})$	12	0	-4	-4	4
$\chi_R(\text{Cs})$	12	0	-4	-4	4
$\chi_R(\text{Mo})$	12	0	-4	-4	4
$\chi_R(\text{O})$	48	0	0	0	0
$N_R(\text{P})$	28	12	12	12	12
$N_R(\text{S})$	12	12	12	12	12
$N_R(\text{S-V})$	04	0	0	0	0
$\chi_R(\text{N})$	84	0	-12	-12	12
$\chi_R(\text{T})$	36	0	-12	-12	12
$\chi_{R(\text{trans})}$	3	0	-1	-1	1
$\chi_R(\text{T}')$	33	0	-11	-11	11
$\chi_R(\text{R}')$	12	0	0	0	0
$\chi_R(\text{n})$	39	0	-5	-5	5

Irreducible representations:

$$\chi_{\text{Li}}^i = 4F_2; \chi_{\text{Cs}}^i = 4F_2; \chi_{\text{Mo/W}}^i = 4F_2; \chi_{\text{O}}^i = 2A_1 + 2A_2 + 4E + 6F_1 + 6F_2$$

$$\chi_{\text{CsLiMoO}_4}^i = 2A_1 + 2A_2 + 4E + 6F_1 + 18F_2$$

Accordingly, the total 84 modes belong to $(2A_1 + 2A_2 + 4E + 6F_1 + 18F_2)$ irreducible symmetry species. Translation modes of $\text{Li}^+/\text{Cs}^+/\text{W}^{2+}$ belongs to $4F_2$ whereas those O^{2-} to $2A_1 + 2A_2 + 4E + 6F_1 + 6F_2$, the acoustic modes

belongs to $6F_2$. The analysis also shows contribution from Cs, Li, Mo /W and O atoms to the vibrations of $\text{CsLiMoO}_4/\text{CsLiWO}_4$ crystals. . The internal vibration of $\text{MoO}_4^{2-}/\text{WO}_4^{2-}$; $\nu_1(A_1)$ $\nu_2(E)$ and $\nu_3 / \nu_4(F_2)$ will not get split in this state. However, Factor group splitting may produce bands in polycrystalline material.

3. Experimental

CsLiMoO_4 and CsLiWO_4 are prepared using stiochiometric ratio of Cs_2CO_3 , Li_2CO_3 and WO_3 using standard solid state route. The detailed structural studies are performed to confirm the single phase formation and are reported elsewhere. Infra-red spectra of the powders were measured in KBr pellets using Bruker IFS 66v IR spectrophotometer and in polyethylene. The Raman spectra of the powder were taken on using Dilor Raman Spectrophotometer with Ar^+ laser using 488 nm wavelength with Laser power 200 mW at the sample. Spectral slit width was 4 cm^{-1} and integration time 1 sec.

4. Results & Discussion

The measured room temperature Infra-red spectra of CsLiMoO_4 (CLM) and CsLiWO_4 are compared in figure 2 in 50-500 cm^{-1} range.

Table.4 Assignment of observed Vibrational Modes in $\text{CsLiMoO}_4 / \text{CsLiWO}_4$

CsLiWO_4		CsLiMoO_4		Assignments
IR	Raman	IR	Raman	
	996 (s) 934 (m)		937 (s) 917 (m)	$\nu_1, \text{Mo/WO}_4^{2-}$ $\nu_1, \text{Mo/WO}_4^{2-}$
859 (vs, asym)	846 (w, sh)	849 (vs)	893 (w, sh) 850 (m)	$\nu_3, \text{Mo/WO}_4^{2-}$ $\nu_3, \text{Mo/WO}_4^{2-}$
608 (s)	722 (m)	597 (vww)		$\nu_4, \text{Mo/WO}_4^{2-}$ $\nu_4, \text{Mo/WO}_4^{2-}$
522 (w)		440 (v. broad)		$\nu_2, \text{Mo/WO}_4^{2-}$
491 (w)		333 (vs, asym.)	344 (w)	$\nu_2, \text{Mo/WO}_4^{2-}$
425 (m)			323 (vs)	
357 (m)		212 (vww)	218 (w)	
316 (s)	359 (vw)	175 (vww)		
261 (w)	327 (vs)		144 (vw)	
143 (w)	157 (broad)		119 (w)	
113 (vww)	90 (sh)	71 (vs, b)	84 (m)	
64 (vs)	56 (sh, s)		66 (w)	
-	44			

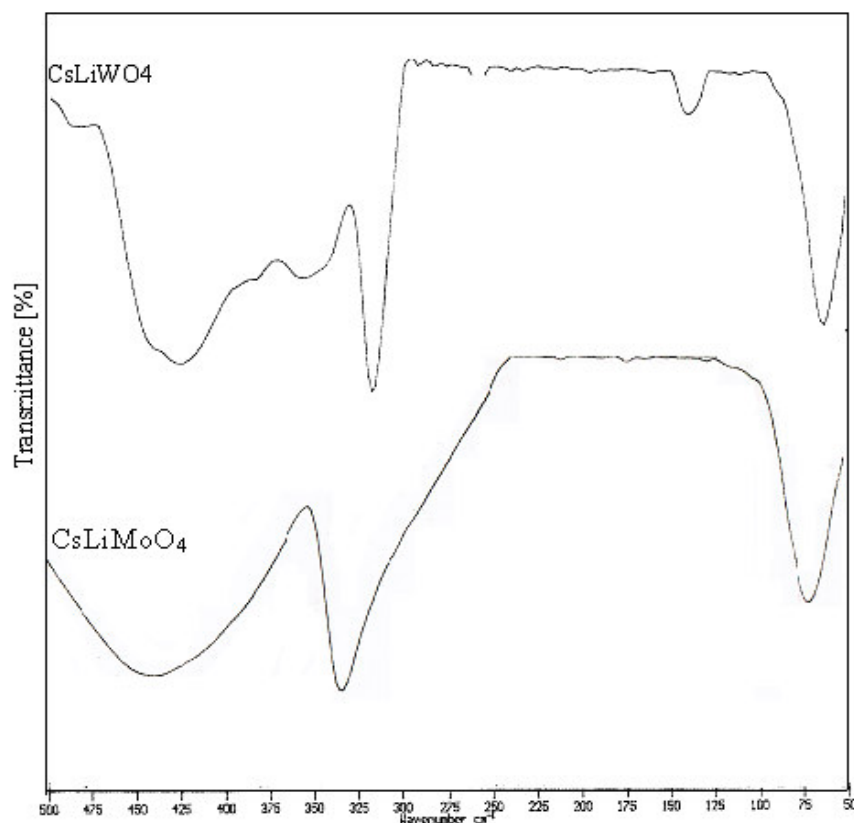


Figure 2 Observed room temperature FTIR spectra of CsLiWO_4 and CsLiMoO_4

Raman shifts in the $30\text{--}1100\text{ cm}^{-1}$ for the two materials are compared in figure 3. Inset shows the Raman spectra in $40\text{--}4000\text{ cm}^{-1}$ range. The observed vibrational modes are shown in table 3. As shown in the figures, Raman spectra do not show any band above 1100 cm^{-1} , whereas bands are seen in IR spectra above this wave number. These are the bands due to the presence of water in matrix used in IR spectra. Thus, the analysis is confined to modes observed up to 1100 cm^{-1} , the range of internal vibrations of tetrahedral unit and the various lattice modes. In double alkali molybdates/tungstates, the effect of size of alkali ions and charge factors are known to influence the spectral features. Therefore, in the analysis an attempt has been made to understand these effects by keeping the ratio of ionic radii of two alkali ions constant. As seen in the figures, the IR and Raman spectra from two materials are almost similar. Thus, the crystal symmetry of two materials is same which is well known in these materials.

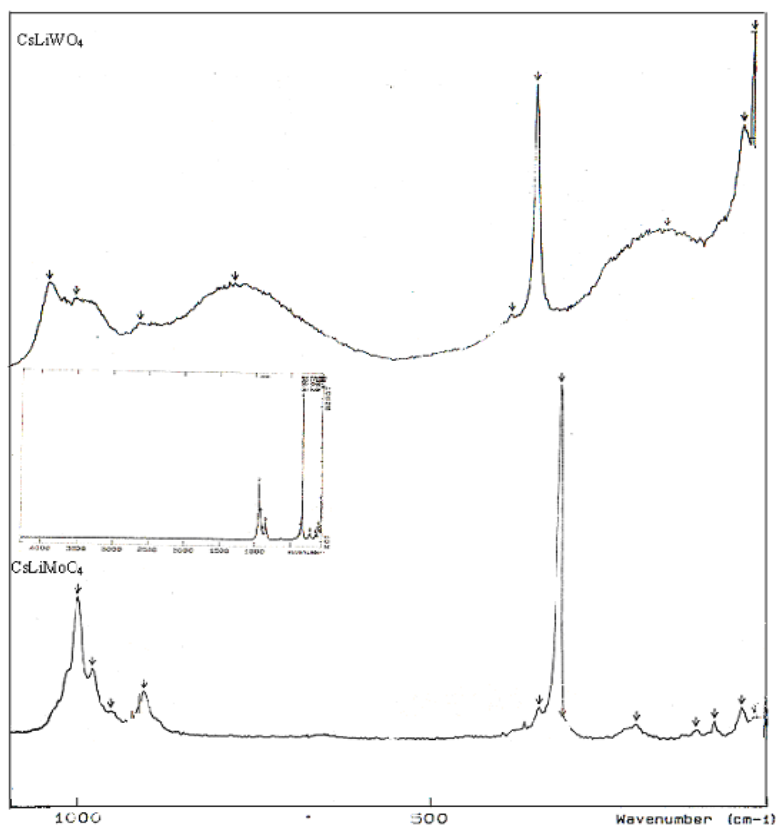


Figure 3: Observed room temperature Raman spectra of CsLiWO_4 and CsLiMoO_4

3.1 Assignments of Vibrational Modes

An isolated tungstates WO_4^{2-} or molybdates MO_4^{2-} has T_d symmetry. The internal vibrations under T_d symmetry transforms as $A_1(\square_1$, totally symmetric bending), $E(\square_2$, asymmetric bending) and $2F_2(\square_3, \square_4$ asymmetric and symmetric stretch). Rotational and translational motions under T_d symmetry transform as F_1 and F_2 species respectively. The rotational and translational motion of the free molecule becomes the librational and translational lattice modes in the crystal. A correlation diagram between molecular point group and unit cell group reveals the splitting of degeneracy's of degenerate modes and the nature of non-degenerate modes. However, in this case it does not give any useful information as the point group symmetry for polyatomic units and unit cell group is same. Thus it is expected that degeneracy will not be lifted. Occurrence of two bands and not four as predicted by FGA means that factor group splitting is not very strong. Further, higher frequency shift in

comparison to free state modes suggest that even though site symmetry is T_d , the oxygen atom disordering is present. The highest frequency range $850\text{--}1100\text{ cm}^{-1}$ is assigned to $\square_1$, totally symmetric stretching of the MO_4^{2-} tetrahedron, the $720\text{--}820\text{ cm}^{-1}$ range belongs to the triply degenerate modes $\square_3$, and the $300\text{--}400\text{ cm}^{-1}$ range contains the doubly ($\square_2$) and triply ($\square_4$) degenerate deformation vibrations of MO_4^{2-} . The range below 200 cm^{-1} belongs to external crystal vibrations—the translational modes of A^+ , B^+ and MO_4^{2-} and the librational modes of MO_4^{2-} .⁶⁻⁹ It is evident from the table, the internal vibrations; especially $\square_1$ and $\square_3$ are sensitive to charge/size effect¹⁰. The ionic radii of Cs is $1.67\text{ \AA}$ and that of Li is $0.67\text{ \AA}$; the ratio $r_{\text{ion}}(A^+/B^+)$ is 2.49. It is well known that in $A^+B^{3+}\text{MO}_4$ (CaMoO₄) scheelite structure) the distribution of A^+ and B^{3+} depends upon this ratio. The distribution of ions at Ca position in scheelite structure is statistical if the ratio is less than 1.27 and ordered if it is more than 1.32¹¹. Therefore, in the present case of cristobalite structure, for the ratio as high as 2.49, it is expected to be ordered. Further, it is well known that for ordered structure, the $\square_1$ range shows two narrow intense band. Thus, the bands observed at 996 and 934 cm^{-1} in tungstates and those observed at 937 and 917 cm^{-1} in molybdates are assigned to $\square_1$ modes. The corresponding bands in IR spectra are missing as is expected for totally symmetric modes of tetrahedra at T_d site. Similarly, the strong band at 859 cm^{-1} in IR and at 846 in Raman spectra in tungstates and that the corresponding bands at 849 (IR) and 893 and 850 cm^{-1} in Raman can be associated with $\square_3$ modes from intensity considerations. This clearly infers that alkali ions are ordered in these materials.

The bands at 316 , 356 cm^{-1} and around 425 cm^{-1} with strong asymmetry at 440 cm^{-1} are observed in the IR spectra of CLW; the corresponding spectral features in CLM are at 440 and 333 cm^{-1} with the later having strong asymmetric feature at around 300 cm^{-1} . The Raman spectra gives strong band at 323 cm^{-1} with a very weak feature at 344 cm^{-1} in CLW and at 328 and 360 cm^{-1} in CLM. These bands are associated with $\square_2$ and $\square_4$. A strong band at 721 cm^{-1} is seen only in CLM Raman spectra are however not seen in CLW. The lattice modes in case of CLM are well resolved whereas for CLW we get a broad band. Whereas, the $\square_4/\square_2$ components are resolved in CLW but show broad band in CLM; $\square_2$ is asymmetric. The reason for this may lie in the charge controlled interaction that may differ in two materials. In an ordered structure, the coulomb interaction between A^+ , B^+ ions, the most probable way of ordering is such that each ion of the same type is surrounded (in the second coordination sphere) only by the ion of other type. This may lead to the lowering of effective site symmetry and splitting of $\square_1$ modes. A careful examination of the intensity and band

splitting pattern of internal modes in two materials suggests that this interaction is more pronounced in molybdates than in tungstates. This is just opposite to what is reported for A^+ , B^{3+} ions interaction with tungstates and molybdates. The role of factor group splitting can also not ruled out at this stage, as the $\square_3$ band in IR and Raman differs significantly (13 cm^{-1}) in tungstates, whereas there is virtually no factor group splitting in molybdates. More careful experiments are needed to further understand this point.

4. Conclusions

Room temperature infra-red and Raman spectra of double alkali tungstates and molybdates having large and small alkali ions are reported and analyzed using group theoretical approach. The detailed factor group analysis is made and the symmetry species associated with internal and external crystal modes are presented based on cubic space group. The effect of the large ratio of the alkali ions radii on the charge ordering is investigated and the observed splitting in $\square_1\square\square\square\square_3$ modes infers that the alkali ions are ordered in the materials. However, the interaction between alkali ions and tungsten/molybdates are different resulting into different spectral features in them.

References

1. V. V. Trunov, V. A. Efremov and Yu. A. Velikondy, *Crystal chemistry and properties of double molybdates and tungstates (in Russian)* Nauka, Leningard (1986).
2. K. S. Aleksandrov, A. T. Anistratov, S. V. Melnikova, P. V. Klevtsov, A. I. Kruglik and V. N. Voronov, Ferroelectric phase transitions in CsLiMoO_4 single crystals, *Physica Status Solidi*, (a) **67** (1981) 377-380.
3. P. Becker, L. Bohatý, R. Fröhlich, H. J. Eichler, K. Ueda, K. Takaichi, J. Hanuza, M. Maczka, H. Rhee and A. A. Kaminskii, Non-centrosymmetric molybdates CsLiMoO_4 and $\text{CsLiMoO}_4 \cdot \frac{1}{3}\text{H}_2\text{O}$: crystal growth, polymorphism, efficient Stokes and anti-Stokes generation and cascaded self-frequency [$\mathcal{X}^{(3)}(\text{SRS}) \rightarrow \mathcal{X}^{(2)}(\text{SFM})$] conversion effects, *Physica Status Solidi*, (a) **202** (2005) 2543-2564.
4. I. N. Flerov, A. V. Kartashev and S. V. Mel'nikova, Calorimetric and optical studies of orthorhombic and cubic CsLiCrO_4 crystals, *Physics of the Solid State*, **48** (2006) 1063-7834.
5. Fang Lie, Bing Yan, Hao Hong Chen and Jing Tai Jhao, Surfactant assisted hydrothermal synthesis of Eu^{3+} doped white light hydroxyl sodium itrium tungstates microspheres and their conversion to $\text{NaY}(\text{WO}_4)_2$, *Inorganic Chem.*, **48** (2009) 7576-7584.
6. K. Okada and J. Ossaka, Crystal data and phase transition of KLiWO_4 and KLiMoO_4 , *J. Solid State Chemistry*, **37** (1981) 325-327.

7. V. A. Kolesov and L. P. Kozeeva, *Raman study of cation distribution in the Scheelite like double molybdates and tungstates*, Zhurnal Strukturnoi Khimii, **34** (1993) 52-58 (Translated by Plenum Publishing).
8. A. A. Kaminskii, L. Bohaty, P. Becker, P. Held, H. Rhee, H. J. Eichler and Hanuza, *J. Trigonal $\text{Na}_3\text{Li}(\text{MoO}_4)_2$ - a new many-phonon SRS molybdate crystal offering numerous nonlinear-laser interactions: several cascaded lasing effects and more than sesqui-octave Stokes and anti-Stokes comb generation*, LASER PHYSICS LETTERS, **6**(2009)335-350.
9. S. Meister, B. Franke, C. Scharfenorth, and H. J. Eichler, Fabrication of tunable band pass filters for CWDM applications }, PLASMA PROCESSES AND POLYMERS, **6** (2009) 727-730.
10. R. F. Klevtsova, L. P. Kozeeva and P. V. Klevtsov, *Kristallographia*, **19** (1974) 89-94.
11. R. D. Shannon, *Acta Crystallogr*, **A32** (1976) 751-767.