



Growth, structural and spectroscopic studies on L-proline lithium bromide monohydrate (LPLBM): a new noncentrosymmetric semiorganic material

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Abstract: Good quality single crystal of L-proline lithium bromide monohydrate (LPLBM) have been grown (size=15×6×5 mm³) for the first time by slow cooling technique. The crystal structure was confirmed by powder X-ray diffraction study and observed that the titled compound is crystallized in monoclinic system with space group *P2₁*. The lattice parameters were refined by CHECKCELL and POWDERX software's and found to be in close agreement with the reported one. Fourier transforms Raman spectroscopy was done for the titled compound in the range of 5-3500 Cm⁻¹ and confirms its formation by observing the fundamental vibrational modes. The ultra violet-visible and near infrared absorption spectroscopy measurement was carried out which shows that the grown crystal is having very less absorbance and confirms its colorless nature. Optical transmission was calculated and reveal that the grown crystal is highly transparent i.e. 78 % in entire testing range. The titled compound was found to be of direct band gap category and its optical band gap was found to be ~5.71eV.

Keywords: L-proline lithium bromide monohydrate; vibrational analysis; thermal properties; optical properties

1. INTRODUCTION

In current past the search of new materials like from organic, inorganic and semiorganic class with unique optical properties is in progress. The use of optical materials has been increased due to their wide range of applications in the field of semiconductors, superconductors, photonics such as high-speed information processing, frequency conversion, optical communication, high optical disk data storage etc. Semiorganic materials have potential to combine the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of the inorganic materials¹⁻⁶. Therefore, in this direction the wide investigation has resulted in the discovery of a series of new semiorganic materials. Current literature survey shows that the various amino acids offer a wide range of choice to synthesize the new semiorganic materials exhibiting enhanced nonlinear optical properties^{7,8}. Some crystals of amino acid complexes with the simple inorganic salts show interesting

physical properties from application point of view. Among the various amino acids, all except the glycine, are distinguish by chiral carbons, acarboxyl (-COOH) and amino (-NH₂) group which are defined as the proton donating and proton accepting molecules. Proline is a rich amino acid in collagen and is exceptional among the amino acids because it is the only one in which the amine group is part of a pyrrolidine ring, thus making it rigid and directional in biological systems⁹. L-proline is widely used for synthesizing a variety of salts with different class of inorganic and acids organic like: L- proline cadmium chloride monohydrate (LPCCM), L-prolinium picrate, L-proline lithium chloride monohydrate (LPLCM), L-proline dimercuricchloride etc, these crystals exhibit good relative second harmonic generation (SHG) efficiency while comparing with KDP^{5,7-12}. L-proline has also been used in various fields like: as a catalyst in different reaction, in preparation of nanoparticle, in Pharmaceutical etc. for different applications¹³⁻²⁰. The metal ions or atoms occurs

extensively in coordination with proteins and show a wide range of functions²¹⁻²³.

Recently a new compound of L-proline with lithium bromide (LPLBM) was synthesized and its crystal growth, crystal structure, spectroscopy, elemental analysis and thermal properties were reported²⁴. It is clear from the current available literature²⁴ on the titled compound that there is no report available on its crystal growth by slow cooling technique, structural by powder X-ray diffraction, FT-Raman spectroscopy analysis so far. The main aim of authors is to explain the above said properties of the titled materials.

Therefore, in the current work the authors are reporting the above said properties of LPLBM so that it can get more clear view on its properties to be used for fabrication of optical devices and the obtained results have been discussed.

2. EXPERIMENTAL

Crystal Growth

To grow the high quality single crystals of titled materials first it was synthesized according to our previous report²⁴.

Then the synthesized material was recrystallized three times to increase the purity of material because the quality of single crystals is based on the purity of material. The saturated solution of LPLBM (~250 ml) was prepared at 30 °C by continuous stirring for more than two days according to its solubility curve²⁴. After that the prepared solution was filtered with whatman filter paper in another perfectly cleaned beaker and covered with Aluminium foil. For slow evaporation of solvent few micron size holes were made in the aluminium foil which results in good quality crystal growth. The covered beaker was then kept in a constant temperature bath of accuracy (± 0.001 °C) at the same temperature (30 °C), after 12h we have started to reduce the temperature of the bath at the rate of 0.03 °C/h and continuously watched with the help of microscope. The first nucleation was start after three days then the temperature reduction was reduced to 0.001 °C/h for further growth. The good quality single crystals of were harvested from the mother solution after 15 days as shown in Fig. 1.



Figure 1. As grown single crystals of LPLBM from slow cooling technique
Characterizations

Powder X-ray diffraction patterns were recorded for pure L-proline as well as L-proline lithium bromide monohydrate (LPLBM) crystals by using Bruker D8 advance powder X-ray diffractometer with $\text{CuK}\alpha_1$ ($\lambda=1.54056$ Å) radiation with scan rate of 0.001 °/s for angular range of 2θ (20-60°) to confirm the crystal system, lattice parameters and formation of compound.

To confirm the crystal formation and study the vibrational modes of LPLBM single crystals the FT-Raman spectrum was recorded in efficiency as well as in fluorescence mode. The laser beam was made to incident normally on the prominent surfaces of the crystal specimens and scattered intensity was collected at 300K using THREMO SCIENTIFIC, DXR FT-RAMAN spectrometer coupled with microscope using full range grating (3500–5 cm^{-1}), laser power 2 mW, wavelength 532 nm filters and estimated resolution was 5.1 to 8.3 cm^{-1} was employed at 300K. The size of the aperture pinhole was set to 50 μm . The optical transparency of LPLBM single crystal of thickness ~ 1.5 mm was recorded by using a JASCO V-570 UV-VIS-NIR spectrophotometer in the wavelength region 190-2500 nm at 300K.

3. RESULT AND DISCUSSION

Structural confirmation

Powder X-ray diffraction patterns of L-proline as well as LPLBM were recorded to know the crystal system and lattice parameters. The confirmation of the titled compound was done by comparing the X-ray diffraction patterns of both the materials. Diffraction patterns shown in Fig. 3 (a) and (b) clearly indicates the formation of the compound.

The recorded X-ray diffraction data was used for lattice parameter refinement purpose by different software's and confirms that the system of the grown crystal is monoclinic with space group P21. The obtained cell parameter of LPLBM using CHECKCELL and POWDERX are presented in Table 1 and found in close agreement with reported data²⁴. The observed value of hkl, 2θ , and d of diffraction peaks of LPLBM are publicized in Table 2.

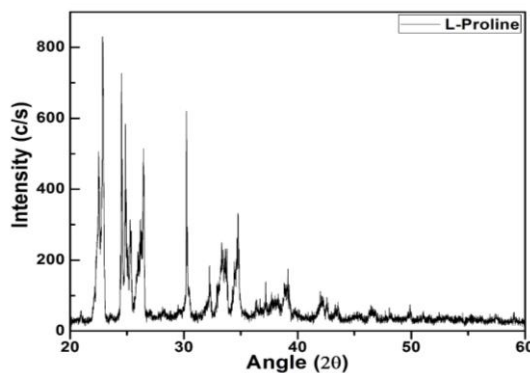


Figure 2. Powder X-ray diffraction patterns of (a) L-proline lithium bromide monohydrate (LPLBM) and (b) pure L-proline

Table 1: Calculated as well as reported Lattice parameters of LPLBM crystals.

| Reported work (LPLBM) | | Current work (LPLBM) | |
|-----------------------|-------------|------------------------------------|--------------------------------------|
| Lattice parameters | [24] | Powder XRD refined data by POWDERX | Powder XRD refined data by CHECKCELL |
| a | 8.0347(7) Å | 8.000430 Å | 8.0343 |
| b | 5.1469(4) Å | 5.132631 Å | |

Table 2: Observed hkl, 2θ(obs.), 2θ(cal.) and d values of LPLBM crystals

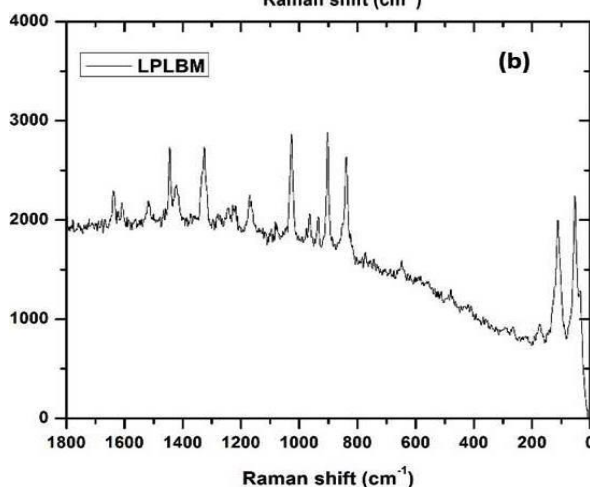
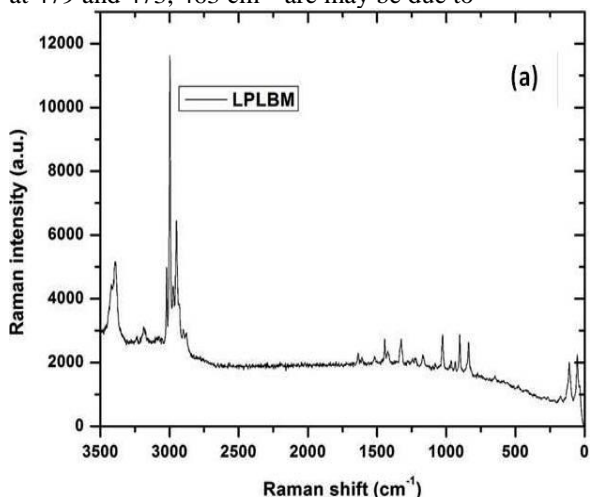
| h | k | l | 2θ(Obs) | 2θ(cal) | d |
|----|---|---|---------|---------|--------|
| 0 | 1 | 1 | 20.801 | 20.737 | 4.2669 |
| -1 | 1 | 1 | 21.420 | 21.362 | 4.1450 |
| -1 | 0 | 2 | 22.459 | 22.411 | 3.9555 |
| 2 | 0 | 1 | 23.040 | 23.005 | 3.8571 |
| 1 | 1 | 1 | 23.621 | 23.567 | 3.7635 |
| 2 | 1 | 0 | 24.526 | 24.512 | 3.6267 |
| -2 | 1 | 1 | 25.224 | 25.199 | 3.5279 |
| -3 | 0 | 1 | 25.755 | 25.726 | 3.4563 |
| 3 | 0 | 0 | 26.069 | 26.030 | 3.4154 |
| 1 | 0 | 2 | 26.496 | 26.483 | 3.3613 |
| -1 | 1 | 2 | 28.456 | 28.426 | 3.1341 |
| 2 | 1 | 1 | 28.925 | 28.904 | 3.0843 |
| -3 | 0 | 2 | 30.284 | 30.263 | 2.9489 |
| -2 | 1 | 2 | 30.669 | 30.647 | 2.9128 |
| -3 | 1 | 1 | 31.174 | 31.148 | 2.8667 |
| 3 | 1 | 0 | 31.415 | 31.404 | 2.8453 |
| 1 | 1 | 2 | 31.776 | 31.786 | 2.8138 |
| 2 | 0 | 2 | 32.143 | 32.162 | 2.7825 |
| -1 | 0 | 3 | 33.568 | 33.578 | 2.6676 |
| -4 | 0 | 1 | 33.952 | 33.969 | 2.6383 |
| 0 | 0 | 3 | 34.678 | 34.680 | 2.5847 |
| -3 | 1 | 2 | 35.017 | 35.048 | 2.5604 |
| 1 | 2 | 0 | 36.055 | 36.046 | 2.4891 |
| 2 | 1 | 2 | 36.725 | 36.726 | 2.4452 |
| 1 | 0 | 3 | 37.906 | 37.906 | 2.3717 |
| -4 | 1 | 1 | 38.322 | 38.344 | 2.3469 |
| 1 | 2 | 1 | 38.566 | 38.607 | 2.3326 |
| 2 | 2 | 0 | 39.197 | 39.220 | 2.2965 |
| 4 | 0 | 1 | 39.594 | 39.599 | 2.2744 |
| -4 | 1 | 2 | 41.005 | 41.020 | 2.1993 |
| 3 | 0 | 2 | 42.661 | 42.654 | 2.1177 |
| 1 | 1 | 4 | 43.336 | 43.330 | 2.0862 |
| 0 | 0 | 5 | 43.939 | 43.940 | 2.0590 |
| 2 | 2 | 1 | 44.212 | 44.210 | 2.0469 |
| -2 | 0 | 5 | 44.384 | 44.380 | 2.0394 |
| 2 | 0 | 4 | 46.821 | 46.819 | 1.9387 |
| 0 | 1 | 5 | 47.524 | 47.525 | 1.9117 |
| 2 | 2 | 2 | 48.041 | 48.040 | 1.8923 |
| 1 | 0 | 5 | 48.388 | 48.382 | 1.8795 |
| -4 | 1 | 2 | 49.034 | 49.035 | 1.8563 |
| -3 | 2 | 1 | 49.053 | 49.056 | 1.8556 |
| -3 | 0 | 5 | 49.212 | 49.220 | 1.8500 |
| -4 | 1 | 0 | 50.051 | 50.052 | 1.8209 |
| 4 | 1 | 0 | 50.051 | 50.052 | 1.8209 |
| 0 | 2 | 4 | 50.084 | 50.086 | 1.8198 |

| | | | | | |
|----|---|---|--------|--------|--------|
| -4 | 0 | 4 | 51.366 | 51.367 | 1.7773 |
| 1 | 1 | 5 | 51.736 | 51.730 | 1.7655 |
| -3 | 2 | 3 | 52.446 | 52.448 | 1.7432 |
| 2 | 2 | 3 | 53.270 | 53.271 | 1.7182 |
| 1 | 2 | 4 | 53.634 | 53.630 | 1.7074 |
| -1 | 1 | 6 | 54.811 | 54.810 | 1.6735 |
| -1 | 3 | 2 | 56.836 | 56.835 | 1.6186 |
| 1 | 0 | 6 | 57.749 | 57.750 | 1.5951 |
| 1 | 3 | 2 | 58.809 | 58.806 | 1.5689 |
| -4 | 1 | 5 | 59.474 | 59.473 | 1.5529 |

FT-Raman spectroscopic analysis

The recorded FT-Raman spectrum of L-proline lithium bromide monohydrate (LPLBM) crystal is shown in Fig. 3 (a) from higher (3500 cm⁻¹) to lower (5 cm⁻¹) range. For more clarity the close view of Raman spectrum has been drawn in to other ranges viz. 3500-2800 cm⁻¹ [Fig. 3(b)] and 1800-5 cm⁻¹ [Fig. 3(c)]. All the observed vibrational modes with their appropriate assignments are explained here. All the Raman peaks are tentatively assigned with the help of other L-proline compounds^{7,8,10}. The broad peak with a shoulder at 3419 and 3399 in Raman spectrum are assigned to stretching vibrations of H₂O (O-H) group. The asymmetric vibration of NH₃ was observed as a broad peak at 3186 cm⁻¹. The NH₃⁺ stretching vibration was observed at 3020 cm⁻¹. Nearly six CH stretching vibrational modes were observed in the range of 3000–2800cm⁻¹ and they are assigned as ν_a(CH₂) at 2996 (very strong peak) and 2972, at 2950, 2928 (shoulder), 2901 cm⁻¹ (low intensity peak) assigned as (νCH) in the spectrum as methylene group. No intense peak was observed in the wavenumber range of 2800-1980 Cm⁻¹. Raman vibrational modes at 1777, 1758, 1722 cm⁻¹ are may be observed due to ν_s(CH₂) vibrations. In the range of 1712–1500 cm⁻¹ region the bending mode of NH₂/NH₂⁺ in plane deformation and H₂O molecules are observed at 1711, 1690, 1677 and 1667, 1638, 1625, 1620, 1609, 1592, 1586, 1576, 1563, 1548, 1541, 1518, 1513 cm⁻¹ as medium and weak intensity bands respectively. While many absorption peaks were observed in the range of 1500–1000cm⁻¹ in Raman spectrum respectively and are assigned as COO⁻ antisymmetric stretching ν_a at 1500 and 1478 cm⁻¹, symmetric stretching ν_s(COO⁻) at 1444, 1421 cm⁻¹, low intensity bending vibration δ(CN) at 1373 and 1363 cm⁻¹, δ(CH₂⁺) vibrations at 1326 cm⁻¹, wagging mode of ω(CH₂) at 1296, 1290, 1280 and 1272, 1266 cm⁻¹ with low and high intensities, torsion vibration of τ(CH₂) group at 1242, 1235 and 1228, 1218 cm⁻¹, rocking mode vibration of r(NH₃⁺) at 1170 and 1163 (shoulder) cm⁻¹, ω(NH₂) at 1124, 1107, 1095, 1088, 1081, 1077 and 1055 cm⁻¹ and ν_a(CN) stretching at 1026 and 1009 cm⁻¹ are may be the main characteristics of LPLBM crystal. In the last more meaningful region related to LPLBM compound band assignments from 1000–400 cm⁻¹ are explained as: ν(CC) vibrations are observed at 975, 964, 946 and 934, 886, 878 and 866 cm⁻¹. The vibrational modes of γ(COO⁻) is observed at 840 cm⁻¹. The vibration modes observed at 783(very low), 773, 743, 733, 722 and 728 and 719 cm⁻¹,

are may be due to $\nu(\text{CH}_2)$ and ν_a of (CONH_2) respectively. While the δ_a , δ_s and ν modes of (COO^-) are obtained at 687, 675, 665, 648 and 626, 618, 603, 598 and 590, 583, 574, 562, 555 and 543 cm^{-1} with low and high intensity. The vibration modes assigned at 479 and 473, 463 cm^{-1} are may be due to



$\nu(\text{COO}^-)$. The vibration modes in the lower range of spectrum were observed at 266, 173, 110 and 53 cm^{-1}

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which are may be due to skeletal vibrations modes of bending.

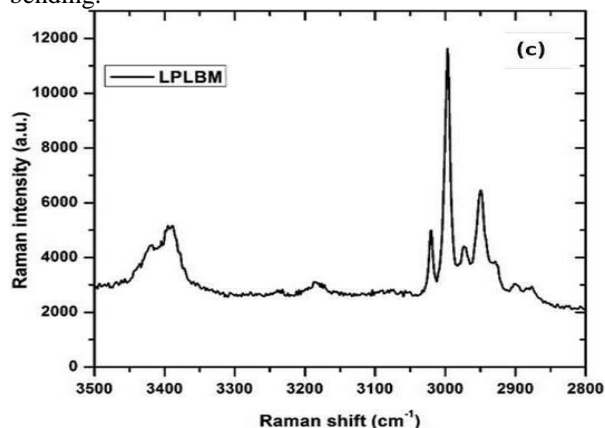


Figure 3. FT-Raman spectra of LPLBM crystal UV-vis-NIR spectroscopic analysis

The recorded absorbance spectrum of LPLBM is shown in Fig. 4(a) which shows that the crystals are very less absorptive and colorless in nature. The cut off wavelength was observed to be at 221 nm. The optical transparency, band gap etc. of the grown crystals were calculated using the absorbance data. Fig. 4(b) shows that the grown crystals are highly transparent in the entire test wavelength and found to be comparable with the earlier reports on titled as well as other materials^{10,24-27} also. High transmission or low absorbance of the grown single crystals in the entire range guarantee the suitability of titled crystals for various optical as well as second harmonic generation (SHG), applications. To study the band structure and types of transitions of electrons in the LPLBM crystal the dependency of optical absorption coefficient (α) on the photon energy ($h\nu$) helps.

The optical band gap (E_g) of the grown crystals was calculated as follows:

By using the absorbance data the optical absorption coefficient (α) was calculated using the relation:

$$\alpha_{crys} = 2.303 \frac{\text{Absorbance } (A_{crys})}{\text{thickness of the crystal } (t_{crys})} \quad (1)$$

where t is the thickness of the used crystal. E_g was calculated from the optical absorption coefficient (α) near the absorption edge according to the relation:

$$(\alpha h\nu)^{1/n} = A [h\nu - (E_g)_{crys}] \quad (2)$$

where A is a constant, h is the plank's constant, ν is the frequency of incident photon and n is an index that differentiates the process of optical absorption in the crystal. Its value is corresponds to 2, 1/2, 3 or 3/2 for indirect allowed, direct allowed, indirect forbidden and direct forbidden transitions, respectively. The E_g of LPLBM crystal was determined at all the transition values of n to confirm that the grown crystal comes in direct band gap material category. E_g of LPLBM crystal was obtained by extrapolating the straight line in the plotted graph to the x-axis $(h\nu)^{28,29}$ as shown in Fig. 5 and from figure it is clear that the best fitting is at $n = 1/2$, which represent to direct allowed transition in LPLBM crystal and the value of band gap is found to be $\sim 5.71 \text{ eV}^{24}$. Such large value of band gap of the titled material suggests that this crystal can be used as a better candidate for optoelectronic applications³⁰.

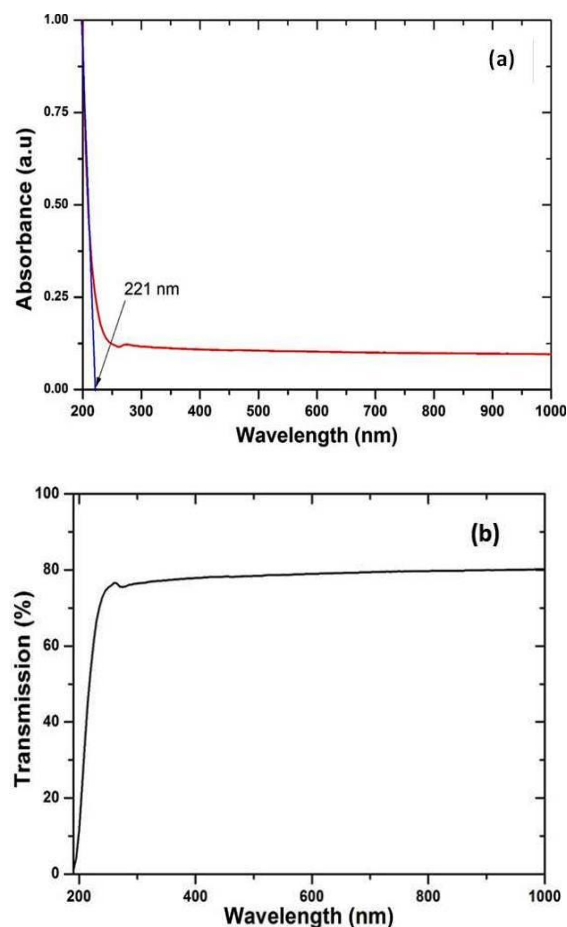


Figure 4. UV-VIS-NIR (a) absorbance and (b) transmittance of LPLBM crystal.

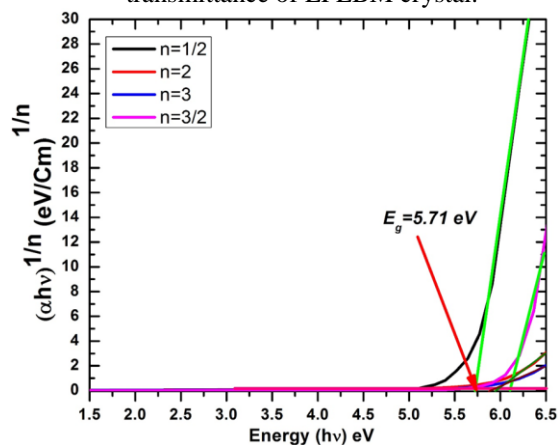


Figure 5. Optical band gap of LPLBM crystal calculated for all transition values of n .

4. CONCLUSIONS

Single crystal of L-proline lithium bromide monohydrate (LPLBM) of size = $15 \times 6 \times 5$ mm³ was grown successfully by slow cooling technique for the first time. The compound/

crystal formation, crystal system and lattice parameters were confirmed by powder X-ray diffraction and further by FT-

Raman spectroscopic analysis. The vibrational modes observed in Raman spectra clearly indicate the formation of L-proline lithium bromide monohydrate (LPLBM) crystal. The optical study suggests that the grown crystal is having good crystalline perfection as the transparency is very high i.e. ~78% in the entire testing range. The optical band gap was calculated and found to be ~5.71 eV which suggest that the materials can be a good candidate for optoelectronic devices. It is found that the LPLBM are optically transparent in wide range which designates its use for nonlinear and other optical applications in various optoelectronic, electro-optic devices.

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