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## Raman and IR Spectra of Pure and Doped Forsterite Single Crystals

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**Abstract:**

*Forsterite single crystals were grown by the Czochralski technique in air. The lattice parameters were determined by X-ray powder diffraction. The IR and Raman spectra of pure and doped ( $V^{3+}$ ,  $V^{5+}$ , and  $Ni^{4+}$ )  $Mg_2SiO_4$  single crystals were measured at room temperature. We studied the phonon properties and discussed the influence of dopants.*

**Keywords:** *Forsterite; X-ray diffraction; IR spectra; Raman spectra; Optical properties.*

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### Introduction

The most abundant mineral in the lower part of the transition zone of the earth,  $\alpha$ - $Mg_2SiO_4$  (forsterite) has extremely low electrical conductivity, low dielectric-constant  $\epsilon_r$ , and low dielectric-losses. These properties make forsterite an ideal substrate and buffer layer material for microwave devices [1]. When it is doped by chromium, forsterite is used as an active medium for solid state lasers [2]. This important discovery has prompted the investigation of its spectroscopic properties. Aside from exploring optical properties in the visible range, special attention has been paid to vibrational spectra, particularly to the local  $A_1$  mode which plays an important role in the mechanism for non-radiative deexcitation in the  $^3T_1$  crystal field (CF) state [3]. This mode is also the only local one involved in the vibrational progression observed in the low temperature optical spectra [4]. The aim of this work is to study the phonon properties of pure and doped  $Mg_2SiO_4$  single crystals (dopants  $V_2O_3$ ,  $V_2O_5$ ,  $NiO_2$ ) in order to provide more understanding of the vibrational structure of this well-known crystal.

### Experimental

Forsterite single crystals were grown from a stoichiometric melt by the Czochralski method from indium crucibles using RF heating. All crystals were grown on seeds oriented along the  $a$ -axis ( $P_{bnm}$  notation). The pulling rate was 3 mm/h and the rotation rate 12 rpm.

The dopant concentration was 1 wt. %, as usually taken in the case of forsterite. The dopant concentrations were checked by microprobe analysis.

The chemical composition was determined by XRD on powders. A Phillips 1710 diffractometer with the radiation  $\lambda_{CuK\alpha_1} = 0.15405$  nm source and original APD software was used. The samples were pressed into standard aluminium frames and the measured range

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for  $2\theta$  was from  $10^\circ$  to  $100^\circ$ . The spectra were obtained at the step of  $0.02^\circ$ . For production identification, the MPDS program and JCPDS (ASTM) card files were used.

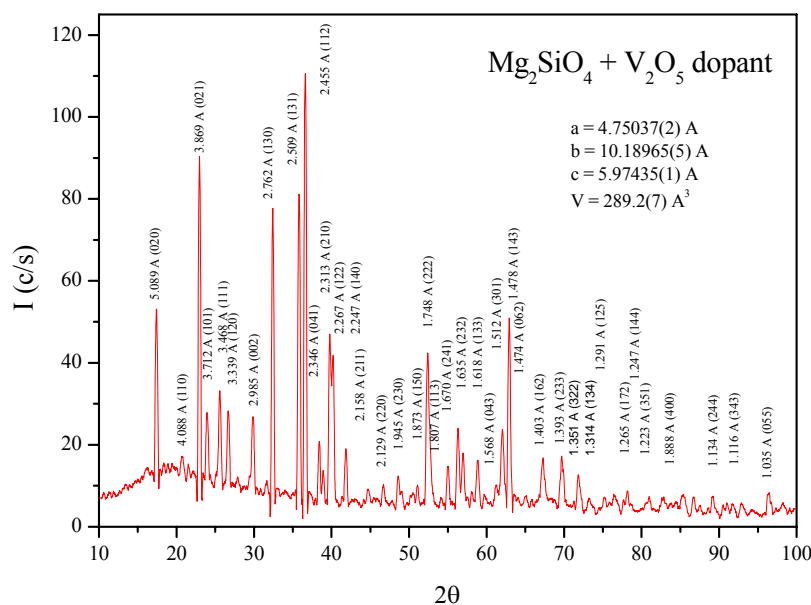
The infrared spectra were recorded using a Bomem DA8 Fourier-transform spectrometer. A wide-range hypersplitter was used for the far infrared region (from  $20$ - $700$   $\text{cm}^{-1}$ ) and a standard KBr ( $400$ - $5000$   $\text{cm}^{-1}$ ) one for the mid infrared region. All the spectra were recorded at a near normal incidence at room temperature. The measurements were performed using a Janis STDA 100 cryostat, which enabled the precise exchange of the sample and the mirror at the same spot on the cold finger.

The Raman spectra were measured at room temperature using a T64000 Jobin-Yvon triple monochromator coupled with a liquid- $\text{N}_2$ -cooled charge-coupled device detector. The Raman scattering measurements were performed in a backscattering configuration. The  $514.5$  nm line of an argon ion laser with output power of  $50$  mW was used. The laser spot size on the sample surface was obtained by a microscope setup with  $10\times$  objective magnification.

## Results and Discussion

Forsterite, a member of the olivine family, has an orthorhombic lattice structure with the space group  $P_{bnm}$  ( $a = 4.76$  Å,  $b = 10.22$  Å,  $c = 5.99$  Å). In the lattice,  $\text{Mg}^{2+}$  ions are in two crystallographic positions, 4a and 4c, which have inversion and mirror point symmetry, respectively.  $\text{Si}^{4+}$  ions are in the 4c position with mirror point symmetry. The  $\text{Si}^{4+}$  tetrahedron connects with two types of  $\text{Mg}^{2+}$  octahedrons.

Unit cells of pure and doped  $\text{Mg}_2\text{SiO}_4$  were calculated by the least square method using 39 reflections. All the reflections correspond to  $\text{Mg}_2\text{SiO}_4$  crystal with parameters of the orthorhombic unit cell:  $a = 0.4765$  (6) nm,  $b = 1.023$  and  $c = 0.5997$  (7) nm [5]. Our calculated results for the lattice parameters of doped forsterite are  $a = 0.4752$  (2) nm,  $b = 1.0191$  (1) nm,  $c = 0.5977$  (1) nm for  $\text{V}_2\text{O}_5$  dopant,  $a = 0.475037$  (2) nm,  $b = 1.01896$  (5) nm,  $c = 0.59744$  (1) nm for  $\text{V}_2\text{O}_5$  dopant, and  $a = 0.4453$  (2) nm,  $b = 1.0187$  (1) nm,  $c = 0.5976$  (1) nm for  $\text{NiO}_2$  dopant, which are in good agreement with the published data. An X-ray diffractogram for powdered  $\text{Mg}_2\text{SiO}_4$  is given in Fig. 1.

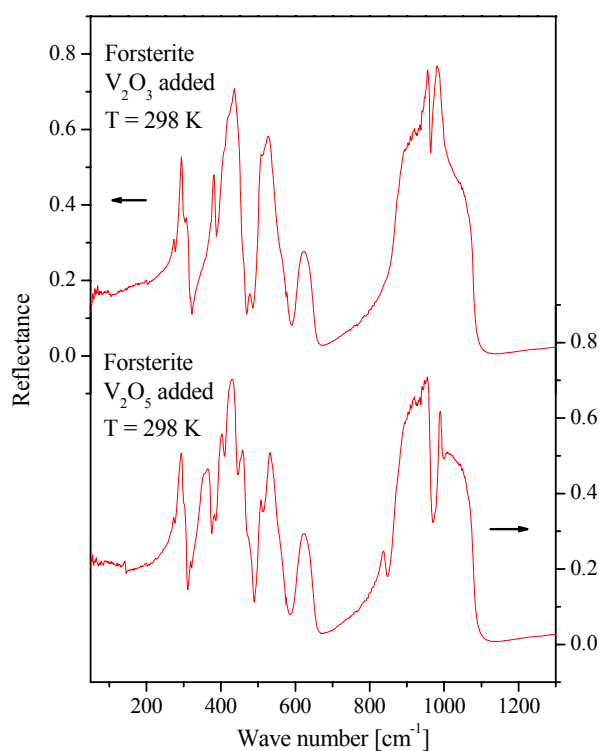


**Fig. 1** X-ray pattern of a powdered  $\text{V}_2\text{O}_5$  doped  $\text{Mg}_2\text{SiO}_4$  single crystal.

Forsterite host  $\text{Mg}_2\text{SiO}_4$  enables vanadium ions to be present in different oxidation states and structural localization. In the crystal structure of forsterite there are two types of Mg-octahedra which distort symmetries  $C_i$  ( $M_1$ ) and  $C_s$  ( $M_2$ ), as well as Si-tetrahedra that is distorted the  $C_s$  symmetry. The octahedra  $M_1$  have a smaller size, than  $M_2$ . The ionic radii of the host and dopant ions are the following: 0.72 and 0.64 Å for octahedral  $\text{Mg}^{2+}$  and  $\text{V}^{3+}$ , respectively, and 0.40, and 0.54 Å for the tetrahedral coordinated  $\text{Si}^{4+}$ , and  $\text{V}^{5+}$ , respectively [6], whereas  $\text{Ni}^{4+}$  substituted the tetrahedral coordinated  $\text{Si}^{4+}$  (ionic radius 0.69 Å).

The covalence effects have been partially taken into account by the potential bending of valent angle O-Si-O and by the assumption about polarizability of oxygen ions. In the case of heterovalent substitution it was supposed, that an excess charge is compensated by the formation of magnesium vacancies (in the sites  $M_1$ , as energetically most favorable).

Fig. 2 represents IR spectra of forsterite single crystals doped with  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ , respectively.



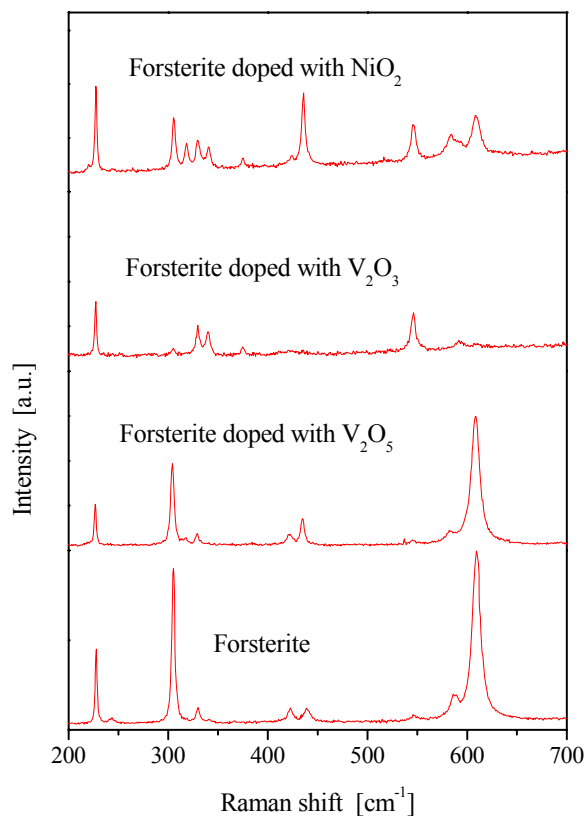
**Fig. 2** Reflectance spectra of  $\text{Mg}_2\text{SiO}_4$  single crystals doped with  $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  in the range 50-1300  $\text{cm}^{-1}$  at  $T=298$  K.

It could be seen from Fig. 2 that differences induced from various dopants ( $\text{V}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ ) are between wave numbers 365 and 476  $\text{cm}^{-1}$ . For dopant  $\text{V}_2\text{O}_3$  impurity three modes appear at 380, 438 and 476  $\text{cm}^{-1}$ , while for dopant  $\text{V}_2\text{O}_5$ , the modes appear at 365, 402 and 459  $\text{cm}^{-1}$ , and an additional one at 836  $\text{cm}^{-1}$ . The last one belongs to  $\text{O}^{2-}$  vibrations in the  $\text{SiO}_4$  group, while the others can be assigned to cation bonds. The mode at 954  $\text{cm}^{-1}$  is split probably due to anharmonicity. Forsterite has partly covalent bonding and this must be taken into account.

The irreducible representation of the forsterite contains 81 vibrational modes [7]:

$$\Gamma = 11A_g + 11B_{1g} + 7B_{2g} + 7B_{3g} + 10A_u + 9B_{1u} + 13B_{2u} + 13B_{3u}$$

where all even vibrations are Raman active while odd vibrations are IR active (the center of inversion is present in the crystal).



**Fig. 3** Raman scattering spectra of pure and doped forsterite single crystals.

Fig. 3 clearly shows Raman spectrum of forsterite. Some differences can be seen around  $300\text{ cm}^{-1}$  due to doping. These modes can be addressed to cation bonds. Some new modes appeared, while, on the other hand, some were missing. The mode at  $\sim 588\text{ cm}^{-1}$  shifted around  $10\text{ cm}^{-1}$  due to dopants ( $586\text{ cm}^{-1}$  for pure forsterite, and  $582$ ,  $584$  and  $592\text{ cm}^{-1}$  for  $\text{NiO}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{V}_2\text{O}_3$ , respectively). This mode belongs to the  $\text{SiO}_4^{2-}$  group and it is strongly affected by doping.

## Conclusion

IR spectra of pure and doped forsterite single crystals have been studied in the range  $50$  to  $5000\text{ cm}^{-1}$ . We especially paid attention to the influences of cations  $\text{V}^{3+}$ ,  $\text{V}^{5+}$ , and  $\text{Ni}^{4+}$  on phonon properties of forsterite in the range  $365$  to  $476\text{ cm}^{-1}$ . The mode at  $954\text{ cm}^{-1}$  is split probably due to anharmonicity.

Raman spectra of pure and doped forsterite single crystals showed differences around  $300\text{ cm}^{-1}$ . In addition, the mode at  $\sim 588\text{ cm}^{-1}$  shifted for  $10\text{ cm}^{-1}$ .

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**Садржај:** Монокристали форстерита су расли из раступа на ваздуху по методи Чохралског. Параметри кристалне решетке су одређивани помоћу методе дифракције X-зрака праха. Инфрацрвени и Раман спектри чистог и допираног ( $V^{3+}$ ,  $V^{5+}$ , and  $Ni^{4+}$ ) монокристала  $Mg_2SiO_4$  су измерени на собној температури. Ми смо проучавали фононске особине и дискутовали смо утицај допаната.

**Кључне речи:** форстерит; дифракција X-зрака; инфрацрвени спектри; Раман спектри; оптичке особине.

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