

# Absorption properties of synthetic Cr-doped spinels in the UV, visible and infrared range and their astronomical implications

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## Summary

Among the oxides, spinels are relatively abundant constituents of stardust, as has been inferred from studies of presolar grains in meteorites. Up to now, only pure Mg–Al-spinels have been considered as a possible stardust component. However, cosmically abundant transition metals such as iron or chromium may well be incorporated in spinels in the process of their formation in stellar atmospheres. We have produced synthetic Cr-doped spinels in order to study their UV, visible and IR spectra. Mass absorption coefficients (MACs) have been derived from transmission spectroscopy over a large wavelength range. For a Cr content of 5%, a maximum MAC in the UV (close to 200 nm) of 1000 cm<sup>2</sup>/g was found. For a Cr content of 10%, the maximum UV-MAC of spinel exceeds the maximum IR-MAC of 2000 cm<sup>2</sup>/g. The MIR bands of Cr-doped spinels are shifted to longer wavelengths with increasing Cr content, namely by ~0.1 μm per 5% Cr in the range covered by our measurements. We conclude that a Cr content of spinel amounting to a few percents (<10%) is compatible with astronomical observations of spinel-bearing dusty environments, while a larger chromium content of spinels is not consistent with the presently available astronomical data.

## Introduction

In the cooling outflows of evolved giant stars, at temperatures around 800–1200 K and pressures of the order of 10<sup>-10</sup> bar, small solid particles (“dust grains”) are formed. These partially crystalline dust grains absorb the stellar radiation in the

UV, visual and near-infrared spectral ranges and re-emit the absorbed energy at mid- and far-infrared wavelengths. The lattice vibrations which take place within these small (typically sub- $\mu\text{m}$ -sized) particles produce characteristic patterns of spectral features – broad emission and/or absorption bands – especially at wavelengths between 7 and 100  $\mu\text{m}$ .

The minerals condensing from the gas phase in stellar outflows need to be highly refractory (such as some oxides, carbides and, partly, carbon itself), and they are primarily composed of elements which are abundant according to the mean cosmic element abundance (e.g. O, C, Mg, Si, Fe, Al, Ca, etc.).

Within the past decades, it has become possible to analyse the mineralogical composition of the dust shells surrounding the aforementioned red giant stars as well as the dust clouds ejected by comets and solid, partially crystalline grains in other cosmic environments. Astromineralogy – the discipline devoted to this analysis – uses three principal methods: *infrared spectroscopy*, in-situ-analysis of *presolar grains* in meteorites and *thermodynamical calculations* aimed at predicting the composition of the various populations of cosmic dust (see, e.g., *Kwok, 2004; Henning, 2003*).

Among circumstellar oxide dust grains, magnesium–aluminium spinels represent a comparatively abundant component. This has been inferred from studies of presolar grains (e.g. *Zinner, 2003; Hoppe, 2004; Mostefaoui and Hoppe, 2004*), and with some provisos it can also be inferred from spectroscopic investigations of the mass loss ejecta of stars on the Asymptotic Giant Branch (*Posch et al., 1999, Fabian et al., 2001*). The abundance of presolar spinel dust inferred for some meteorites is the highest abundance of O-rich dust found in meteorites to date (*Mostefaoui and Hoppe, 2004*). Presolar spinel appears to be as abundant as presolar graphite and is not as rare as has previously been assumed. By spectroscopic methods and calculations according to the Mie theory, it has been shown by *Fabian et al. (2001)* that small, approximately spherical grains composed of  $\text{MgAl}_2\text{O}_4$  have their emissivity maxima at 13, 16.8 and 32  $\mu\text{m}$  (769, 595 and 312  $\text{cm}^{-1}$ ). The precise positions of these infrared bands depend on the stoichiometry (i.e. Mg:Al ratio) of the spinels, on the particle shape and on the grain temperature. Furthermore, the conditions of the formation of the spinels (especially the formation temperature) also influence the band pattern. As was pointed out by *Fabian et al. (2001)*, there is a remarkable coincidence between the infrared bands of synthetic, nearly stoichiometric Mg–Al-spinels and the 13, 16.8 and 32  $\mu\text{m}$  dust emission spectra of several oxygen-rich red giant stars. However, as *Sloan et al. (2003)* have shown, the 16.8  $\mu\text{m}$  emission band in the spectra of Asymptotic Giant Branch stars may be due to  $\text{CO}_2$  rather than to spinel. These authors do not find any correlation between the intensities of the 13 and 32  $\mu\text{m}$  bands in the spectra of circumstellar shells, which makes it questionable whether these bands can indeed be assigned to spinel.

Even though the spectroscopic evidence for Mg–Al-spinels in circumstellar dust is not unambiguous at the moment and even though there is no evidence for Cr-doped spinels in cosmic dust, it is still desirable to examine them from the astronomer’s point of view, namely for the following reasons. (i) Among the astronomically relevant transition metals chromium is the second most abundant one (see Table 1). (ii) Chromium is easily incorporated into spinels (see below).

Table 1. *Cosmic elemental abundances (according to Lodders, 2003). The abundances are normalised to a value of  $\log \varepsilon = 12$  for hydrogen. The second column refers to elemental abundance derived from analyses of CI chondrites. The third column refers to elemental abundances in the sun*

Element	Log $\varepsilon_{\text{chondrites}}$	Log $\varepsilon_{\text{solar}}$
Mg	7.56	7.54
Fe	7.48	7.45
Al	6.46	6.47
Cr	5.66	5.64
Mn	5.50	5.39

(iii) Variations in the chromium concentration have a major influence on the absorption properties in the VIS/NIR range and, hence, also an influence on the radiative equilibrium temperature of spinels containing Cr.

The present paper is an extension of the study by *Fabian et al. (2001)* towards chromium-doped spinels. The underlying question is the following: Given that nearly stoichiometric Mg–Al-spinels have infrared bands which permit a good reproduction especially of the above mentioned 13  $\mu\text{m}$  emission band of cosmic dust, to which extent is this also true for Cr-doped spinels? Which chromium content of spinels is still compatible with the astronomical spectra?

A further point of astromineralogical interest is how the UV/VIS/NIR mass absorption coefficient (MAC) of spinels can be increased (given that pure Mg–Al-spinel is very transparent in the visible and adjacent range of the electromagnetic spectrum). Since chromium belongs to the transition metals, Cr-doping is quite an efficient way of increasing the absorption coefficient of spinel and, hence, a potential way of increasing equilibrium temperature of spinel in a stellar radiation field. Mn, Cr and Fe are the only transition metals with significant mean cosmic elemental abundances (see Table 1, where we compare the abundances of Mn, Cr and Fe with those of Mg and Al). The concept of cosmic elemental abundance is very important as a constraint for the formation of solid particles in circumstellar environments. Many mineral forming elements such as e.g. titanium are so rare according to the cosmic elemental abundance that their refractory solid compounds (e.g.  $\text{CaTiO}_3$ ,  $\text{TiO}_2$ ) can only be minor components of cosmic dust, representing certainly much less than 1% of its total mass.

## Experimental

In order to produce chromium doped-spinels, we mixed MgO-,  $\text{MgAl}_2\text{O}_4$ - and  $\text{Cr}_2\text{O}_3$ -powders to homogenous samples according to the respective required stoichiometric proportions between these precursor materials. Chromium oxide is well suited to be incorporated in spinels due to the fact that this chemical compound has the same valence as  $\text{Al}_2\text{O}_3$  (e.g. *Ikeda et al., 1997*). Note, however, that natural *terrestrial* spinels of  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$  composition are rather rare. Cr-rich terrestrial spinels – chromites – are mostly of  $(\text{Mg,Fe})(\text{Al,Cr})_2\text{O}_4$  composition, i.e. high concentrations of chromium are found only in iron-bearing spinels.

Table 2.  $\text{Cr}_2\text{O}_3$  contents of samples studied as derived from energy-dispersive X-ray analyses and calculated spinel formulae

$\text{Cr}_2\text{O}_3$ concentration [wt.%]	Chemical formula
1.35	$\text{Mg}_{0.93}\text{Al}_{1.99}\text{Cr}_{0.03}\text{O}_4$
6.43	$\text{Mg}_{0.98}\text{Al}_{1.89}\text{Cr}_{0.12}\text{O}_4$
11.64	$\text{Mg}_{0.98}\text{Al}_{1.78}\text{Cr}_{0.23}\text{O}_4$

Using a microbalance, we produced three different Cr-doped spinels with different chromium concentration with the general chemical formula  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$ ,  $x$  amounting to 0.03, 0.12 and 0.23 (Table 2). These rather low chromium concentrations have been chosen in order to meet the constraints set by the cosmic elemental abundances, according to which aluminium is about six times more abundant than chromium (e.g. *Lodders and Fegley, 2003*) (the most Cr rich of the samples that we synthesized has a  $\text{Cr}_2\text{O}_3$  content of 11.6 wt%, corresponding to  $x = 0.23$ ).

Our powder samples (dark-green due to the presence of  $\text{Cr}_2\text{O}_3$  powder) were pressed to pellets which were then melted using an Arc-Melting-Device (Bühler MAM-1) to produce a crystalline droplet. After the melting procedure we obtained three compounds that indeed showed the cubic spinel structure, as has been inferred from the respective subsequent X-ray analyses. The colours of the droplets significantly differ from those of the initial powders: they vary from red in the chromium-poor  $\text{Mg}_{0.93}\text{Al}_{1.99}\text{Cr}_{0.03}\text{O}_4$  spinel to dark red, almost black, in  $\text{Mg}_{0.98}\text{Al}_{1.78}\text{Cr}_{0.23}\text{O}_4$ . Such colours are typical of Cr-bearing spinels of  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$  compositions, wherein it is caused by electronic spin-allowed d-d-transitions in octahedral  $\text{Cr}^{3+}$  (e.g. *Wood et al., 1968*). Also, the colour-change evidences that chromium enters into the structure predominantly as  $\text{Cr}^{3+}$  in the octahedral sites of the spinel structure. Transition metal ions of electronic  $d^3$ -configuration have high crystal field stabilisation energy in octahedral ligand surrounding. Thus,  $\text{Cr}^{3+}$ , which has three  $d$ -electrons above an argon-like electronic shell (e.g. *Marfunin, 1979*), prefers octahedral coordination. In natural minerals, for instance, trivalent chromium ions always occupy octahedral sites. There are no known examples of  $\text{Cr}^{3+}$  entering tetrahedral sites in natural minerals (e.g. *Burns, 1993*).

The produced  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$ -samples have the structure of an ordinary spinel but with partial inversion: A fraction of the  $\text{Al}^{3+}$  ions occupies tetrahedral vacancies due to the high formation temperature (see *Andreozzi et al., 2000*, for the temperature dependence of the degree of inversion).

The melting droplets were then ground to powders with typical grain sizes of about 1–2  $\mu\text{m}$ . The chromium-spinel powder was subsequently embedded in a matrix of potassium bromide with a ratio of 1:500 and finally pressed to pellets. The exact chemical formulae of the chromium spinels, as shown in Table 2, were calculated from energy-dispersive X-ray (EDX) analyses, where 12 spots of each of the three pellets were scanned and investigated for inhomogeneities and variations in the Mg/Al/Cr ratios.

The transmittance of these powder pellets in the UV/VIS/NIR wavelength range (0.275 to 2  $\mu\text{m}$ ) was measured with a Perkin Elmer spectrometer

Lambda 19 together with an integration sphere which allowed us to quantify the transmittance without any scattering losses.

The MIR (7–25  $\mu\text{m}$ ) powder transmission spectra were measured using a Bruker FTIR 113v spectrometer. After the first spectroscopic investigations the transmittance spectra exhibited  $\text{H}_2\text{O}$  features. Therefore the powders were tempered at 210  $^\circ\text{C}$  in order to evaporate the  $\text{H}_2\text{O}$  contained in the powdered samples.

Additionally, absorption spectra were measured on *thin sections* prepared from the droplets. Depending on the chromium content the thicknesses of the sections were 0.27, 0.11 and 0.08 mm for the samples of  $x = 0.03$ , 0.12 and 0.23, respectively. A single beam optical absorption spectrometer, constructed on the basis of a SpectraPro-275 triple grating monochromator and a highly modified polarising mineralogical microscope MIN-8, were used. Ultrafluars 10 $\times$  served as objective and condenser. Changeable photoelectric multiplying tubes and a cooled PbS-cell were used as photodetectors. A mechanical high-stabilised 300 Hz-chopper and lock-in amplifier were applied to improve the signal/noise ratio. The spectra were scanned with steps  $\Delta\lambda = 1$  nm, 2 nm and 10 nm in the range 350–450, 450–1000, 1000–1500 nm, respectively. The diameter of the measuring spot was not larger than 400  $\mu\text{m}$ .

### Results for the UV/VIS/NIR range

Absorption and transmittance spectra (Figs. 1 and 2, respectively), measured by the two different methods described in the previous section, give rather convergent results. The spectra show an increase of the absorption in the UV/VIS range with increasing chromium concentration, while the materials remain nearly 100% transparent in the NIR range at  $\lambda > 1 \mu\text{m}$  (Fig. 1). Aluminium to chromium substitution results in an increased UV-absorption, seen in the spectra as a short-wave absorption edge, and intensification of two distinct absorption bands around 387 and 550 nm, superimposed by the edge (Fig. 1). The positions and shapes of these

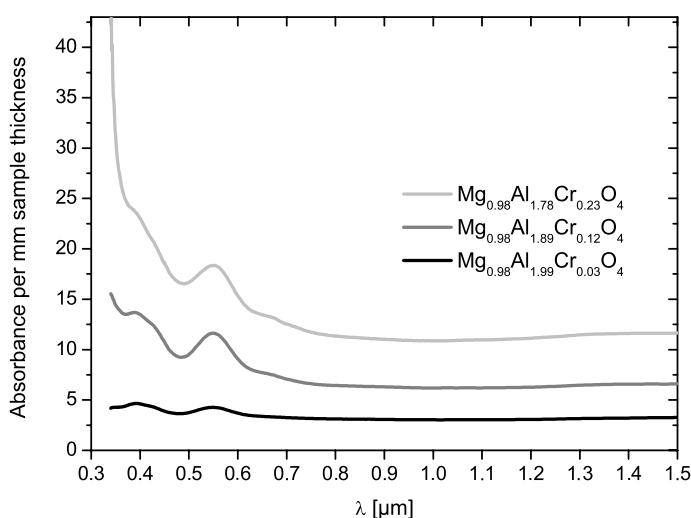


Fig. 1. UV/VIS/NIR absorption spectra of thin sections of Cr-doped spinels

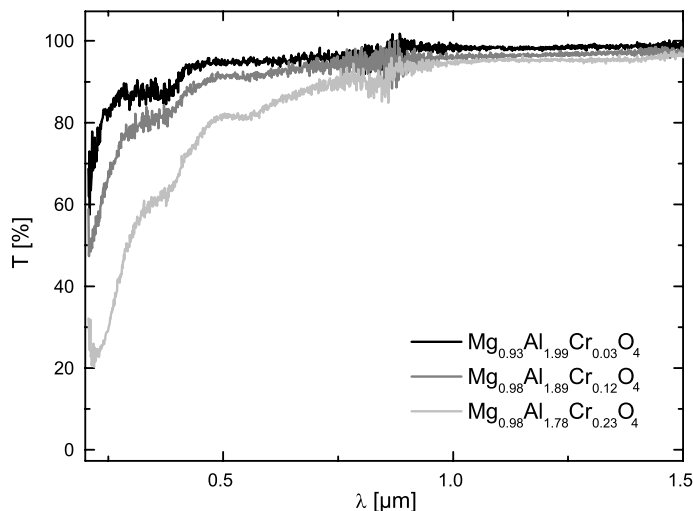


Fig. 2. Transmittance of Cr-doped spinel powders in the UV/VIS/NIR-range

bands are in good accordance with the band positions in crystal-field spectra of low-chromium Mg–Al-spinels, both natural and synthetic, published elsewhere (e.g. *Wood et al.*, 1968; *Taran et al.*, 1994; *Ikeda et al.*, 1997). These bands originate from electronic  ${}^4T_{1g} \leftarrow {}^4A_{2g}$  transitions at 387 nm ( $25850 \text{ cm}^{-1}$ ), and  ${}^4T_{2g} \leftarrow {}^4A_{2g}$ , 550 nm ( $18180 \text{ cm}^{-1}$ ).

From the powder transmittance data (Fig. 2) we calculated the mass absorption coefficient (MAC) using the relation:

$$MAC = -\frac{A_{\text{pellet}} \log T}{m_{\text{pellet}}}, \quad (1)$$

where the MAC is given in units of  $\text{cm}^2/\text{g}$ ,  $T$  is the transmittance,  $A_{\text{pellet}}$  the geometric cross section of the pellet in  $\text{cm}^2$  and  $m_{\text{pellet}}$  the mass of the pellet in g. As the transmittance  $T$ , the MAC depends on the chromium concentration. Therefore the sample richest in chromium has the highest MAC.

### Results for the MIR range; interpretation of the bands and band shifts

The most conspicuous features in the MIR transmittance spectra of Cr-doped spinels are the  $14 \mu\text{m}$  and  $18 \mu\text{m}$  bands (see Fig. 3) which are also characteristic of pure Mg–Al-spinels. As shown by *Preudhomme and Tarte* (1971), these bands mainly originate from vibrations of the trivalent, octahedrally coordinated cation in the spinel lattice (i.e. from an Al–O vibration in the case of Mg–Al-spinels). Our spectra show a shift of the  $14 \mu\text{m}$  and  $18 \mu\text{m}$  bands to longer wavelengths with increasing chromium concentration and a nearly linear correlation between the chromium content and the band displacement (Fig. 4). The displacement of the bands depends on the type of the octahedral, trivalent cation. Since the incorporated Cr-atoms replace some of the Al-atoms in the doped spinels, the type of some of the trivalent cations is thereby changed. Not all aspects of the different nature of Al and Cr contribute to the band shift. The different mass and ionic radius have

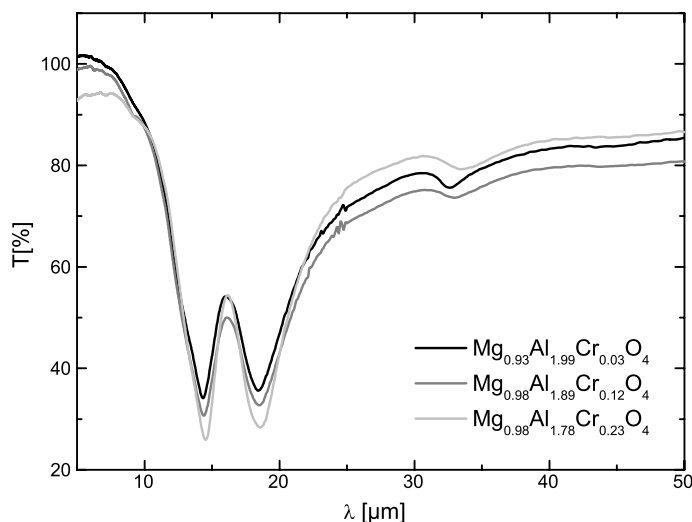


Fig. 3. Transmittance of Cr-doped spinel powders in the MIR range

a minor – if any – influence on the band positions, whereas the different bonding force between oxygen and the octahedral cation is of crucial importance (see *Preudhomme and Tarte, 1971*).

It should be noted that although in synthetic spinels a part of the Al cations occupy tetrahedrally coordinated lattice places, there are no spectral features evidencing any entering of Cr ions into tetrahedral sites of the structure. In accordance with theory (e.g. *Marfunin, 1979; Burns, 1993*) the crystal field strength of a  $3d^N$ -ion in a tetrahedron is  $4/9$  of that in an octahedron. Therefore, for tetrahedral  $Cr^{3+}$ , the expected positions of absorption bands are around  $11500$  and  $8080\text{ cm}^{-1}$  as derived from  $25850\text{ cm}^{-1}$  and  $18180\text{ cm}^{-1}$  of octahedral  $Cr^{3+}$ . Such virtual bands

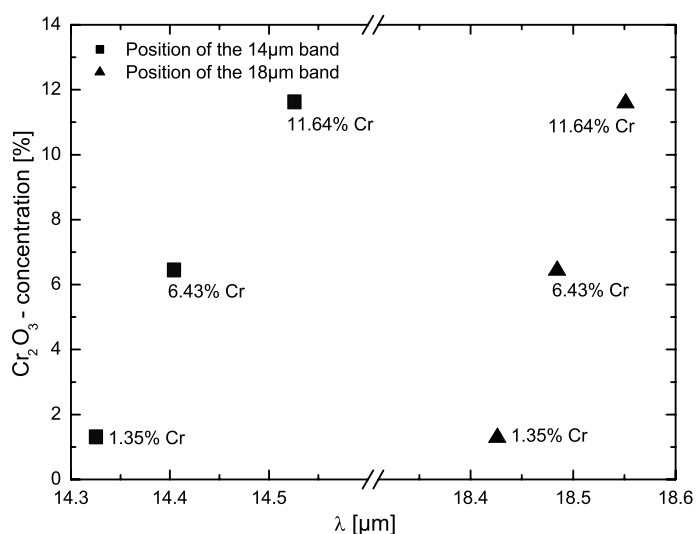


Fig. 4. MIR band positions of Cr-doped spinels. The linear displacement of the  $14\text{ }\mu\text{m}$  and the  $18\text{ }\mu\text{m}$  bands is caused by the increasing chromium concentration of the samples

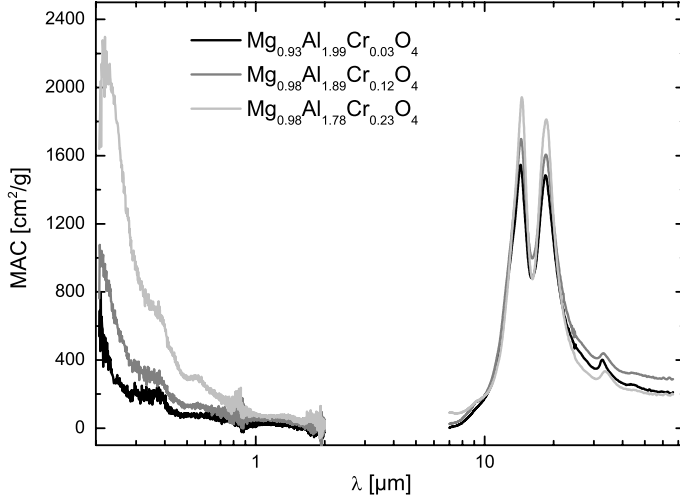


Fig. 5. Mass absorption coefficients of Cr-doped spinels

of tetrahedral  $\text{Cr}^{3+}$  would have been rather intense because of a lack of centre of symmetry in tetrahedral sites (e.g. *Taran and Langer, 2001*). However, as seen from the spectra in Figs. 1–2, there are no bands around  $11500$  and  $8080\text{ cm}^{-1}$  ( $870$  and  $1240\text{ nm}$ , respectively) which could be attributed to  $\text{Cr}^{3+}$  in the tetrahedral sites of the spinel.

The calculation of the mass absorption coefficient from the MIR transmittance data using Eq. (1). shows that the highest chromium concentration leads to the highest MAC peaks at  $14\text{ }\mu\text{m}$  and  $18\text{ }\mu\text{m}$ . Figure 5 presents the combination of the mass absorption coefficient corresponding to the transmittance data plotted in Figs. 2 and 3. These combined data were then used to derive the temperature of spinel dust in circumstellar shells (see below).

## Astrophysical implications

### IR band positions

In previous publications, we have shown that for approximately spherical particles, the main IR band of spinel – arising from Al–O vibrations – is located at  $12.95$ – $13.3\text{ }\mu\text{m}$ . The exact peak position depends on the particle shapes and on the optical constants, which are different for natural, annealed and synthetic spinels. The dependence of the band position on the particle shape is caused by surface modes in small grains, which are of vital importance for the interpretation of stardust spectra. Both annealed and synthetic spinels (i.e. spinels synthesised at high temperatures) can be considered as realistic analogues of cosmic dust grains, since the latter are also formed at high temperatures ( $>1000\text{ K}$ ). For synthetic stoichiometric spinel a position of the MAC of spherical spinel particles of  $12.95\text{ }\mu\text{m}$  ( $772\text{ cm}^{-1}$ ) results from the optical constants published by *Tropf and Thomas (1991)*. For annealed natural spinel with the chemical composition  $\text{Mg}_{1.02}\text{Al}_{1.93}\text{Si}_{0.03}\text{Fe}_{0.01}\text{Cr}_{0.01}\text{O}_4$ , *Fabian et al. (2001)* found a position of the MAC maximum at  $13.1\text{ }\mu\text{m}$  ( $763\text{ cm}^{-1}$ ).



In the light of the present investigation, it appears likely that the difference between the position of the MAC maxima according to *Tropf* and *Thomas* (1991) vs. *Fabian* et al. (2001) is related to the Cr, Fe (and maybe Si) content of the sample used by the latter.

The band positions given above do not coincide with the positions of the absorbance maxima derived from powder transmission spectroscopy. Powders produced by grinding minerals do not consist of spherical grains after all; rather, they typically consist of very elongated splinters. In the case of spinel, this leads to a shift of the band position by 1.3  $\mu\text{m}$  compared to spherical grains, i.e. from 13.0 to 14.3  $\mu\text{m}$  (see *Bohren* and *Huffman*, 1983, and below). In other words, a measured band position of 14.3  $\mu\text{m}$  for powder transmission spectra corresponds to a band position of 13.0  $\mu\text{m}$  for spherical grains in a circumstellar shell.

One of the aims of our investigation was to determine the chromium content of spinels which is still compatible with astronomical observations, assuming the circumstellar spinel grains to be roughly spherical in shape and assuming that (possibly Cr-containing) spinels be the carrier of the 13  $\mu\text{m}$  emission band. As discussed in before the position of the strongest IR band of spinel is shifted to longer wavelengths due to the incorporation of chromium into the crystal lattice. Increasing the Cr content of spinel by 5% leads to a shift of the main band by approximately 0.1  $\mu\text{m}$ . The range of band positions of the astronomical 13  $\mu\text{m}$  band is 12.9–13.1  $\mu\text{m}$  (*Posch* et al., 1999). This variation in band positions of 0.2  $\mu\text{m}$  corresponds to a variation in the Cr content of 10%. Hence, Cr-doped spinels with chromium contents larger than 10% can safely be excluded as carriers of the 13  $\mu\text{m}$  band on the basis of the present investigation and of the presently available astronomical IR spectra.

Figure 6 shows the 13  $\mu\text{m}$  emission band, as detected in the spectrum of the AGB star Y UMa with the Infrared Space Observatory (ISO), compared to the emissivities  $Q_{\text{abs}}$  of small spherical grains with different Cr contents. The latter

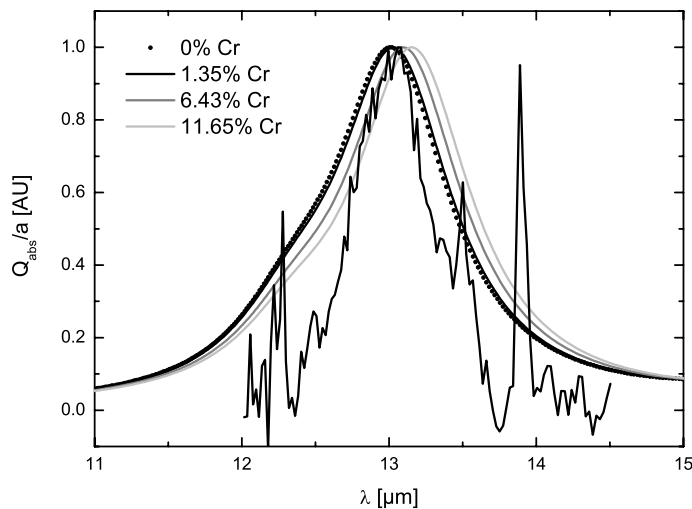


Fig. 6. Comparison of the 13  $\mu\text{m}$  emission band of the AGB star Y UMa with the normalized absorption efficiency of synthetic  $\text{MgAl}_2\text{O}_4$  as well as Cr-doped synthetic Mg–Al-spinels

have been calculated as follows: The Lorentz oscillator data for a Cr-free synthetic spinel published by *Fabian et al. (2001)* have been modified such as to account for the observed shift of the maximum of  $\varepsilon''$  towards smaller wavenumbers (larger wavelengths) due to the incorporation of chromium. The position of the maximum of  $\varepsilon''$  has been assumed to shift in the same proportion as the position of the maximum of the MAC as a function of the Cr content. The calculation of  $Q_{\text{abs}}$  was then performed by using the relation  $Q_{\text{abs}}/a = 8\pi/\lambda * \text{Im}((\varepsilon - 1)/(\varepsilon + 2))$ , where  $a$  is the radius of a grain small compared to the wavelength,  $\varepsilon$  is the complex dielectric function, and  $\text{Im}$  means imaginary part. As can be inferred from Fig. 6, the  $13 \mu\text{m}$  emission band of Y UMa is quite satisfactorily reproduced by the absorption efficiency of small spherical spinel particles with a Cr content of about 5%.

### *Equilibrium dust temperatures*

An important astrophysical application of the measured MAC is the calculation of the temperature of dust grains located in circumstellar shells in order to understand the conditions in dust forming and dust harbouring regions. Assuming a thermodynamic equilibrium between the stellar radiation field and the dust grains, it is possible to derive the dust temperature for a given distance from the star from the energy balance using numerical integration techniques. The radiative energy absorbed is under this assumption given by the integral

$$I_1 = D_{\text{rad}} \pi a^2 \int_0^{\infty} \text{MAC}(\lambda) B(\lambda, T_*) d\lambda. \quad (2)$$

Equation (2), together with the radial dilution factor of the stellar radiation field  $D_{\text{rad}}$ :

$$D_{\text{rad}} = 2 \left[ 1 - \sqrt{1 - \frac{R_*^2}{R_d^2}} \right] \quad (3)$$

describes the energy absorbed by an individual dust grain in a circumstellar shell. The radiative energy emitted by the same dust grain is given by the expression

$$I_2 = 4\pi a^2 \int_0^{\infty} \text{MAC}(\lambda) B(\lambda, T_d) d\lambda. \quad (4)$$

Of course, the integrals  $I_1$  and  $I_2$  cannot be calculated from zero to infinity, but it is sufficient to integrate over all those wavelengths where the star emits significant amounts of energy – i.e. the contribution of far UV and radio wavelengths can be neglected. The combination of these equations leads to Eq. (5), from which the dust temperature finally is calculated:

$$R(T_d) = \left[ 1 - \left( 1 - \frac{2I_2}{I_1} \right)^2 \right]^{-0.5} \quad (5)$$

For the calculation of the temperature properties of our Cr-doped spinels we used the previously derived MAC data together with a stellar surface temperature  $T_*$  of 3000 K. This temperature refers to a typical asymptotic giant branch (AGB) star (cf. *Habing and Olofsson, 2003*).

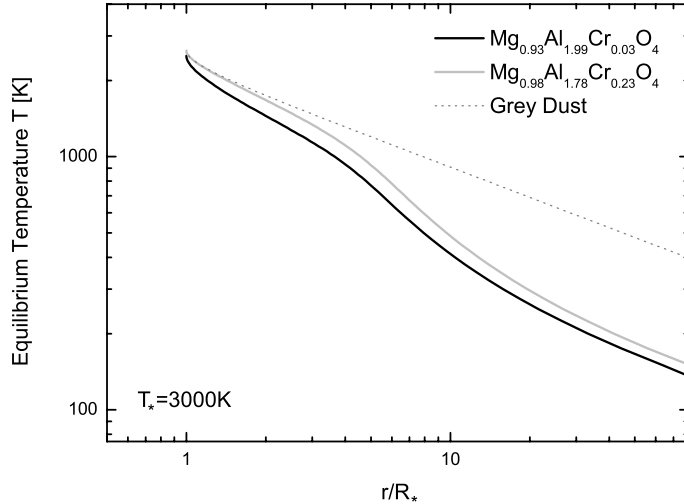


Fig. 7. Equilibrium temperatures of Cr-doped spinel dust grains in a circumstellar shell. A higher Cr content results in a higher equilibrium temperature due to the grain heating by enhanced absorption in the visual and UV range

In Fig. 7, the temperature curves of the spinels with  $\text{MgAl}_{2-x}\text{Cr}_x\text{O}_4$  compositions with 1.35% and 11.64% chromium concentration are plotted together with a grey dust curve. (Grey dust grains are defined as bodies with MACs proportional to  $1/\lambda$  in the IR range). The equilibrium temperatures of the Cr-doped spinels are lower than the temperature of grey dust and show a dependence on the chromium concentration. A high chromium amount results in a higher dust temperature especially in the close vicinity of the AGB star. This effect is due to an increased absorption of light by the Cr-doped spinels in the UV/VIS-range. It may be of significance for the formation of spinels in circumstellar shells: Cr-free (and Fe-free) spinels will have their condensation point closer to the respective “parent star”, where the circumstellar matter is still denser, which makes the condensation process more effective. This may be an explanation for the spectroscopically inferred dominance of almost transition-metal-free spinels in circumstellar shells.

### Concluding remarks

The condensation of spinel grains in cooling outflows of red giant stars with solar elemental abundances was predicted based on investigations of presolar grains in meteorites and on IR-spectroscopic studies of circumstellar dust (even though the latter do not deliver unambiguous information up to now). The incorporation of small amounts of Cr into spinels cannot be ruled out in circumstellar shells, given that these are characterised by an average Cr:Al-ratio of 1:6.3. We therefore studied the effect of Cr incorporation in spinel both on the UV/VIS and on the MIR spectra of spinels, finding that with increasing Cr content, not only a huge increase of the mass absorption coefficient in the UV, but also a shift of the MIR bands to larger wavelengths takes place. Both effects set constraints on the possible Cr content of circumstellar spinel dust grains – at least if these are the carrier of the  $13\ \mu\text{m}$  emission band (the origin of which is still lively debated in the astronomical

literature). Under this assumption, only a Cr content of spinels up to 10% is compatible with current astronomical observations.

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