Photo-Luminescence and Possible Forsterite nanoparticles Model of Extended Red Emission

K. Koike¹, H. Chihara², 4, C. Koike², M. Nakagawa¹, M. Okada³, M. Matsumura¹, and J. Takada³

¹ Faculty of Education, Kagawa University, Takamatsu 760-8522, Japan
e-mail: Koike@ed.Kagawa-u.ac.jp
² Kyoto Pharmaceutical University, Kyoto 607-8412, Japan
³ Research Reactor Institute, Kyoto University, Kumatori 590-0499, Japan
⁴ Department of Earth and Space Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

Abstract. Possible forsterite nanoparticle model of the Extended Red Emission (ERE) is proposed on the basis of photo-luminescence of forsterite after gamma-ray and neutron irradiation. Forsterite exhibits interesting thermoluminescence spectrum similar to ERE of Red Rectangle after irradiation in low temperature. It is shown that the forsterite after thermoluminescence is over exhibits photo-luminescence (PL) when Ultraviolet ray is irradiated. The structure of PL spectrum is almost similar to that of thermoluminescence. In order to explain small variations of the peak position of wavelength of ERE spectrum, possible nanoparticle model of forsterite is investigated. Our model is consistent to the ISO observation data in near and middle infrared region, which suggest the existence of forsterite.

Key words. ISM:dust, extinction – ISM: general – ISM: lines and bands

1. Introduction

Extended red emission (ERE) is a broad emission band with a peak wavelength between 600 and 850 nm, and with a width between 60 and 120 nm seen in many dusty astrophysical objects such as reflection nebulae, planetary nebulae, HII regions, halos of galaxies, and even in the Diffuse Interstellar Medium. The observation of ERE in the Diffuse Interstellar Medium shows that ERE is a general phenomenon. Though the carrier for ERE is not yet clear, the proposed carriers are hydrogenate amorphous carbon (HAC), quenched carbonaceous composite (QCC), C₆₀, carbon nanoparticles, polycyclic aromatic hydrocarbons (PAHs), and silicon nanoparticles, and most of them appear to be unable to explain the observed ERE spectra (see Ledoux et al. 2001; Witt et al. 1998, for a summary).

We have suggested that thermoluminescence spectra of forsterite after γ-ray irradiation are very similar to ERE of Red Rectangle (Koike K. et al., 2002, here after KK), and have discussed such possibility that thermoluminescence is related to the changes of property of interstellar and circumstellar matter by various irradiation in that space. It is, however, not so plausible that the irradiation energy is sufficient to explain such emissions.

Recently, we have found that the forsterite after thermoluminescence is over exhibits photo-luminescence (PL) when ultraviolet ray (UV) is irradiated. This fact seems to suggest a possible realistic mechanism of ERE. This paper is concerning to this problem.

Interstellar and circumstellar matter is irradiated by high energy electromagnetic and cosmic ray particles such as γ rays, neutrons, protons and heavy-ions etc. These irradiation will cause some changes on properties such as optical ones of these materials. Especially, it is known that extremely large fluxes of neutrons and γ-rays have been emitted during super-nova explosions. Furthermore, interstellar and circumstellar space is typically at extremely low temperature and is always irradiated by electromagnetic radiation and by cosmic ray particles for long time-scale. The effect of this radiation will accumulate in the low temperature environment. In the circumstellar region of both young and evolved stars as well as in the solar system, forsterite and enstatite have been found (Waters et al., 1998ab; Malfait et al., 1998; Wooden et al., 1999) by the Infrared Space Observatory (ISO) (Kessler et al., 1996). Carbonates such as dolomite CaMg(CO₃)₂, breunnerite Mg(Fe, Mn)(CO₃)₂, calcite CaCO₃, and Mg,Ca-bearing siderite FeCO₃ were found in CI chondrite (Endress, Zinner and Bischoff, 1996). Among these carbonates, Ca-bearing minerals such as dolomite and calcite
were also detected in dust shells around evolved stars by ISO (Kemper et al., 2002). Especially, it should be noted that the broad emission feature responsible for extended red emission (ERE) appears at about the 600 – 900 nm region in many reflection nebulae, and among reflection nebulae the Red Rectangle nebula shows stronger intensity by one order (Witt and Boroson, 1990). In the Red Rectangle nebula, both PAH- and crystalline silicates (forsterite and enstatite)-features were observed by ISO (Waters et al., 1998b). We have suggested, on the basis of the measurement of thermoluminescence for irradiated silicates and carbonates, our thermoluminescence spectra of forsterite at 645–655 nm is very similar to the ERE of the Red Rectangle (KK, 2002).

In this paper, we will investigate the changes of properties of silicates by irradiation in the context of astrophysics. Especially, it is emphasized that the forsterite after thermoluminescence is over exhibits photoluminescence (PL) when ultraviolet ray (UV) is irradiated. The structure of PL spectrum is almost similar to that of thermoluminescence. Further, possible forsterite nanoparticle model of ERE is also discussed on the basis of this fact.

2. Photoluminescence of forsterite under UV irradiation

We have ever discussed that thermoluminescence spectrum of irradiated bulk samples of forsterite, Mg$_2$SiO$_4$, is very similar to the ERE of Red Rectangle. The samples were irradiated with gamma-rays to a dose of about $10.4 \times 10^4$ Gy (J/Kg) in liquid nitrogen using the $^{60}$Co gamma-ray irradiation facility of Kyoto University Reactor. The gamma-rays of $^{60}$Co have two peaks at 1.1 MeV and 1.3 MeV. Our samples of forsterite were synthesized by Takei and Kobayashi (1974), and Tachibana (2000) using the
CZ (Czochralski) method, with high accuracy. The bulk of the irradiated forsterite is about 138 mg. We have measured the thermoluminescence spectra of these samples using a spectrophotometer (including a CCD camera, from Princeton Instruments, Inc.). The sample is put on a thermally-isolated plate, previously cooled to liquid nitrogen temperature. The luminescence emission during warming is introduced to the CCD measuring system using an optically transparent fiber. We measured the thermoluminescence spectrum of forsterite from liquid nitrogen temperature to about 500K. As is discussed previously, the spectrum is very similar to ERE of Red Rectangle. We have discussed such mechanism that the effect of various irradiation on cosmic matter is accumulated in the extremely low temperature environment of interstellar and circumstellar space, and it will only be observed provided that the condition to release the accumulated energy is realized in circumstellar space. This may occur when irradiated dust moves to a warmer domain in an interstellar or circumstellar environment.

However, amount of irradiation energy seems to be insufficient to explain the large emission energy of ERE. This difficulty will be overcome by taking into account of the interesting fact that we have recently found. That is, the forsterite after thermoluminescence is over exhibits photo-luminescence(PL) when ultraviolet-ray (UV) is irradiated. For the UV-ray source, we have used a mercury lamp.

Fig. 1 shows the photo-luminescence spectra of forsterite (Mg$_2$SiO$_4$) under UV irradiation at room temperature after the thermoluminescence of γ-ray irradiation is over. It should be noted that this spectra is almost similar to that of thermoluminescence, however, the detailed structures of spectrum seems to disappear. Does photoluminescence of forsterite occur when only UV-ray is irradiated without the preceding gamma-ray irradiation on the sample? The answer is no! We have confirmed that any photo-luminescence does not appear for γ-ray non-irradiated forsterite.

Furthermore, at liquid nitrogen temperature we have investigated the effect of UV-ray irradiation on forsterite after thermoluminescence caused by γ-ray irradiation had been over. In this temperature, we cannot find UV photoluminescence. However, when the UV irradiated forsterite is warmed, thermoluminescence spectra similar to the γ-ray irradiated one appears. The UV photo-luminescence spectrum at fixed temperature between the liquid nitrogen and room temperatures are not yet measured, because it is very difficult to hold the sample at the fixed temperature in this range.

It should be emphasized that the existence of UV emission from almost all stars or nebulae is well known fact, and our discovery of UV photo-luminescence of forsterite seems to resolve the problem of energy source. It should be noted, however, that peaks of spectrum of various ERE exhibit small amount of difference. It is just a nanoparticle model of ERE that can explain shift of the peak position of spectrum.

3. Possible silicon nanoparticle model and some problems

It is known that a prominent model of ERE is the silicon nanoparticle model. The general mechanism of PL in solids is summarized as follows. When a photon of energy higher than the so-called band gap of the material (the separation between valence and conduction bands) is absorbed, an electron-hole pair is created. On a very short timescale the energy is thermalized so that the energy separation between the electron and the hole becomes approximately equal to the energy of the gap. Then the pair can radioactively recombine, giving rise to the photo-luminescence. As a result, the peak position of the photoluminescence roughly reflects the band gap of the material. It should be noted that for the energy gap $V_g$ [eV], the corresponding wavelength $\lambda$ [nm] is given as,

$$\lambda = \frac{1234}{V_g}$$

in the degree of $10^{-4}$, as is easily confirmed from $h\nu = E$. Then, the energy gap corresponding to ERE wavelength is about 1.4 - 2.2 eV.

In metals there is no PL because there is no gap. For semiconductor bulk silicon, the energy gap is about 1.17 eV. In nano sized silicon particles, the transition probability is drastically enhanced and the energy gap is extended to ERE range because the surfaces of nanoparticles is completely passivated to avoid quenching the photoluminescence and the spatial confinement is associated with a broadening of the pair state in momentum space.

The most important consequence of the spatial confinement of the electronic wave function in nano sized systems is the progressive widening of the band gap as the particle size is reduced. Theoretical studies have shown (Delerue et al. 1993) in quantitative this remarkable fact in a certain kind of model. The physical meaning of this fact seems to understand by making use of uncertainty principle of quantum system qualitatively. That is, the spatial confinement of the electronic wave function restricts the uncertainty of electron $\Delta X$ to the diameter of restricted size of the nanoparticle, then due to the uncertainty principle,

$$\Delta X \Delta P \geq \hbar$$

the magnitude of $\Delta P$ becomes large. Thus the smaller the size of particles, the larger the energy scale is extended. Does the silicon nanoparticle exist really? It is not probable that all silicons can exist only in nanoparticle state in universe. That is, it is natural to suppose that the conditions to form the more large particles or bulk of silicon will be often realized in universe where embrace various conditions. As discussed before, the energy gap is extended in the nano sized silicon particles. In the more large silicon particles or small bulk, it is expected, from simulation experiments, that the strong emission feature will appear at 16.4 $\mu$m and the peak of silicon spectrum at 20 $\mu$m in the near and middle infrared-ray region. However, both
of them are not yet observed until now. In practice, ISO result show the characteristic four peaks which exhibits the existence of forsterite.

4. Investigation of formation process of Elements, and Silicates

In order to investigate possible existence form of silicates, let us examine the formation process of elements in stars. In the core of proto-star, firstly H burns through the thermo-nuclear fusion. This process proceeds very slowly and He is formed. At a certain temperature, He-burn starts and C and O are produced in the core of star. According to rising the temperature of core, C-burn starts and it produces Mg etc in its core region. Further, O-burn starts and produces Si in the core of star. In a star with heavy mass, Si burns finally in core and produce Fe etc. It should be noted that Si is produced in the core region, which is already surrounded by C and O in its shell structure. Further, in a certain kind of heavy stars, it is known that heavy elements than Fe is produced through the r- and s-processes.

By thermonuclear runaway called as thermal pulses, the entire envelop is mixed efficiently and Si is transported to the surface of the star. Important aspect for stars on the AGB is that these stars lose a large fraction of their mass. The physical mechanism responsible for these high mass-loss is thought to be stellar pulsation in combination with the formation of dust. Further, the stellar wind reduces the envelop mass of star.

From the above summarization of formation condition of dust based on nuclear fusion in star, it seems to be natural to suppose that almost all Si exists in the form of silicates such as SiO$_2$, MgSiO$_3$, Mg$_2$SiO$_4$, or SiC, so far as there is no special mechanism which prevents to make these crystalline.

5. Possible forsterite nanoparticle hypothesis

Why the γ-ray or neutron irradiated forsterite exhibits the photo-luminescence under UV irradiation? Though the change of material property of forsterite by irradiation is not yet clear except that of optical property, it seems that the new energy band-like structure is formed by lattice defects and/or deformations of the structure as irradiation effects. It should be noted that the new energy level or band-like structure is formed by lattice defect in some insulators such as TiO$_2$, and they have properties of semiconductor. The mechanism of UV photo-luminescence of forsterite seems to be realized through the similar mechanism. In order to make clear irradiation effect on forsterite by the method of solid state physics, it is expected to investigate to the change of forsterite structure by both ESR experiments and theoretical approach.

Summarizing our investigation, we will propose possible forsterite model of ERE, in which ERE is caused by UV photo-luminescence of various size of forsterite containing nano size particles, where these forsterite particles have been irradiated by various kind of cosmic-rays. The variety of peak of emission spectrum is due to the existence of nano size particle of forsterite. In fact, the existence of forsterite is confirmed by ISO spectrum.

6. Discussion

It should be noted that interstellar and circumstellar space is typically at extremely low temperature and is always irradiated by both electromagnetic radiation and by cosmic ray particles over cosmological timescales. Furthermore, it is well known that extremely large fluxes of neutrons and gamma-rays are emitted during supernova explosions. We have ever suggested that thermoluminescence spectra of forsterite after γ-ray irradiation are very similar to ERE of Red Rectangle. However, the energy efficiency of thermoluminescence seems to be not sufficient to explain ERE. In this paper, we have discussed on the fact that the photo-luminescence of irradiated forsterite exhibits similar spectrum to that of thermoluminescence. It should also be remembered that forsterite and enstatite have been found by many ISO observations in many oxygen-rich young and evolved stars.

Is the irradiated forsterite possible to be really one of the carrier of ERE? It is possible so far as its temperature is below about 1000 K, because it is known in many insulators the effects of irradiation are almost maintained. However, the irradiation effects on insulators are known to fade out by annealing it to high temperature above this degree. In such case, can forsterite be a carrier of ERE?

In semiconductor silicon, it is well known that the existence of a small amount of impurity caused by a certain kind of minor elements such as As, P, B, Ga or In etc cause new energy levels and forms new type of semiconductors. Though little is known about forsterite, it seems to be possible that a certain kind of impurities cause some semiconductor-like structure of forsterite. Investigation of such possibility is further problem. In this context, it should be noted that the melting point of silicon is 1410 $°$C, while that of forsterite is very high, and is 1890 $°$C. It is known that the existence of forsterite is observed in addition to ISO spectrum, in meteorites, while silicon itself is not found in both of them. Thus, together with the investigation of formation condition of silicates in the previous section, the silicon nanoparticle model seems to be highly hypothetical one in the present stage.

We can get easily high-quality crystalline silicon because it is the most fundamental semiconductor, where the solid state properties is very well studied together with the problem of impurity. As for the forsterite, it is very difficult to get the high-quality one. Then, we have used the synthesized one by CZ method in laboratory. For the impurity component in our forsterite sample, Takei and Kobayashi reported previously that spectrographic analysis shows that the forsterite sample is pure. However, neutron activation analysis reveals that it contains an infinitesimal quantity of Ir at about 16–18 wt ppm. This level of Ir impurity is below the detection limit of spectro-
graphic analysis. We have also measured our sample using radio activation analysis, and confirmed that our sample is almost pure; that is, other elements except for Mg, Si, O and an infinitesimal quantity of Ir are not detected.

In order to confirm the reappearance of thermoluminescence of forsterite in other sample, we have get forsterite powder for china and porcelain from a pottery "Marusu" (Japan), where details of the method of creation of it is not open. We have investigated thermoluminescence of the "Marusu" forsterite, and get almost the same result as our synthesized one.

7. Summary
In this paper, we have discussed about the possibility that the photo-luminescence of irradiated forsterite by γ-ray and cosmic-rays may contribute to ERE. It should also be re-emphasized that forsterite and enstatite have been found by many ISO observations in many oxygen-rich young and evolved stars. It is natural to suppose they assume any responsibility in many phenomena such as ERE. In order to investigate further properties of forsterite, much lot of crystalline forsterite with high-quality is necessary, just as crystalline silicon which is mass-produced as the important material of semiconductor. Synthesizing forsterite and enstatite in laboratory is very restricted in practice. It is expected to investigate properties of forsterite with a certain kind of minor elements as impurity.

It is interesting to suppose the case in which silicon nanoparticles and irradiated forsterite co-exist as the carrier of ERE. In such case, almost all silicon in the circumstellar space should exist as nanoparticle form, while forsterite is possible in various size from bulk to nanoparticle, as is suggested from the restriction of present observation such as ISO etc.

Finally, investigating the detailed structure of change on forsterite by irradiation and possible semiconductor-like structure caused by impurity in the context of astrophysics is further problem.

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