Gamma ray irradiation induced point defects in BaF_2^*

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Abstract There are some original nonmagnetic point defects in the BaF_2 crystallite powder, such as interstitial and vacant F^- which can become paramagnetic centers by γ-ray-irradiation at room temperature. After γ-ray irradiation the paramagnetic point defects V_k, H, F and M centers, have been observed in the sample with experiment of electron spin resonance (ESR). Frenkel exciton, a nonmagnetic point defect, can also be induced by the γ-ray irradiation in the sample at room temperature, the existence of the Frenkel exciton is affirmed by an anomalous change of the ESR signal of V_k center with temperature. The signals of the ESR of the H, F and M centers weaken and vanish with the temperature increasing monotonously. But the ESR signal of the V_k enhances when the temperature goes up about 127°C, then weakens and vanishes. An increase in the V_k center follows an annihilation of the Frenkel exciton with heating.

Keywords Gamma-ray irradiation, Frenkel exciton, Paramagnetic point defect, V_k center

1 Introduction

In many years W. Hayes and P. J. Call *et al.* have devoted themselves to the studies of point defects in alkaline earth fluoride crystals and of defects produced by irradiation[1,2] with electron spin resonance (ESR) method. ESR has been proved to be a very sensitive, reliable and important technique for the studies of point defects in solid materials. The point defects of paramagnetic color centers produced by the γ-ray and X-ray irradiations are mainly: F center (an electron trapped by anion vacancy), V_k center (self-trapped hole center, or a hole trapped by a lattice anion), H center (a hole trapped by an interstitial anion) and M center (adjacency of two F centers). In many cases the V_k center is complementary to the F center[1]. In BaF_2 the F center is an electron trapped by F^- vacancy, the V_k center is a F^0 at lattice site, the H center is a F^0 at interstitial site, and the M center is a pair of electrons trapped by two adjacent F^- ions vacancies.

Barium halide possesses some excellent luminescence properties to which much attention has been paid, they doped with rare earth are being studied widely for the γ-ray detection and X-ray image storage materials. The BaF_2 is a very nice detection material for high-energy particles, its irradiation effect is of considerable interest both from the research viewpoint and that of applications. Its ESR spectra are similar to those of $BaCl_2$. Comparing ESR spectra of $BaCl_2$[3] and BaF_2, we found existence of the Frenkel exciton.

2 Experiments

Three samples are studied. The sample #1 is BaF_2 crystallite powder, the sample #2 is abrasive powder of the BaF_2 single crystal, the sample #3 is BaF_2 single crystal. The ESR experiments were carried out at room temperature, the samples were heated from 18°C to 420°C. The microwave frequency f was 9.4588 GHz. The ^{60}Co source was used for γ-ray-irradiation at room temperature, the radiation dose rate was 103.3 Gy/min.

3 Results and analysis

No ESR signal has been observed before γ-ray irradiation in the three samples, so the ESR signals observed after γ-ray irradiation in the sample #1 and #2 stem from irradiation induced paramagnetic point defects without doubt. There are four peaks in the sample #1 with ΔH_{pp} about 2–4 mT after γ-ray-irradiation for 30 min; there is quite a wide peak in the sample #2 with ΔH_{pp} of 43.5 mT

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for 5 min γ-ray-irradiation. There is still no ESR peak in the sample #3 for 30 min γ-ray-irradiation, the reason might be that the point defects locate often at the surface of grains, the sample #3 is perfect crystal, the surface per unit mass is much less than those of the smaple #1 and #2, and the irradiated defects annihilate below room temperature[1,2]. On the other hand, after γ-ray irradiation, there is still no ESR signal in the sample #3. It is to say, there are original nonmagnetic point defects in the samples of the BaF_2 crystallite powder and abrasive powder of the BaF_2 single crystal, such as interstitial and vacant F^- which are located mainly at the surface and boundary plane of crystallite grains, and these nonmagnetic point defects can become paramagnetic centers by γ-ray-irradiation at room temperature.

The ESR spectra of the samples #1 and #2 at room temperature are shown in Fig.1 and Fig.2. The values of the g factor of the ESR signals are determined with a standard sample DPPH (g=2.0037). These g values are compared with g_e of free electron (2.0023), and with ESR spectra of irradiated $BaCl_2$ crystallite[3]; the four ESR peaks in the sample #1 are affirmed[4], they are V_k (g=2.2022), H (2.0834), F (1.9884) and M [g=(1.9884+1.9426)/2= 1.9655] in the sample #1. The intensities of ESR signals of the H, K and M are weakened with temperature increasing monotonously, and that of H vanishes at 67°C, those of the K and M at 150°C, because the crystalline grain tends to perfection, and the defects annihilate with heating and time[4].

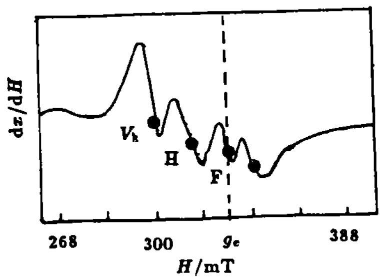

Fig.1 The ESR spectra of BaF_2 crystallite powder (sample #1) after γ-ray irradiation

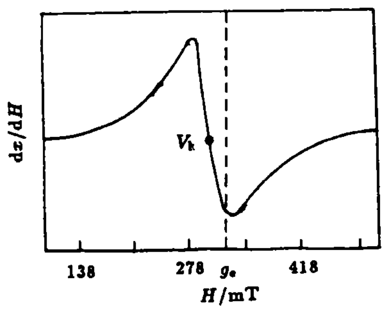

Fig.2 The ESR spectra of abrasive powder of the BaF_2 single crystal (sample #2) after γ-ray irradiation

It is found that the ESR signal of V_k center does not decline monotonously with the temperature increasing as those of the H, F and M centers do, the change of its intensity with temperature is not monotonous, the intensity enhances when the temperature goes up to 127°C (it shows the number of the V_k center increases), then weakens, and vanishes at not higher than 350°C (it is annihilation of the V_k center). The ESR signal of V_k center in $BaCl_2$ is weakened with temperature increasing monotonously, and vanishes at 71°C[3]. The dependences of the intensities of the ESR signals of V_k center in BaF_2 and $BaCl_2$ on the temperature are shown in Fig.3.

The ESR signal is a wide peak with ΔH_{pp} about 43.5 mT and g=2.2212 in the sample #2. The change of intensity of ESR signal with temperature is also not monotonous, the intensity of the signal enhances when the temperature goes up below 100°C, it nearly does not change at 100~ 200°C, then weakens, and vanishes at 420°C. The signal is also of V_k center, the sample #2 is abrasive powder of the BaF_2 single crystal, the anion vacancy is at the surface of the grains, and there is no interstitial anion, so no H, F and M centers. Details of the experiment and analysis are described in Ref.[4].

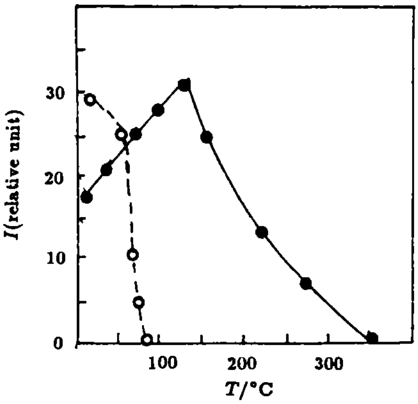

Fig.3 The dependence of the intensities of the ESR signals of V_k center in BaF_2 and $BaCl_2$ on the temperature

Solid line is of BaF_2, the dashed line is of $BaCl_2$

The phenomenon that the ESR signal of the V_k enhances with temperature increasing in the samples #1 and #2, is related to the Frenkel exciton excited by the γ-ray irradiation in BaF_2. C. S. Shi *et al* had found this exciton with experimentation of an absorption spectrum[5], the gap energy is 10.9 eV, and the exciton binding energy is 1.1 eV. A Frenkel exciton is a tightly bound electron-hole pair, it is called an elementary excition or an excited state of a single atom. It is induced as an electron of 2p of F^- ion is excited to a higher level of outer shell orbit by the γ-ray irradiation, and the electron is coupled with the hole of the 2p orbit. When the electron in the Frenkel exciton gets energy from heating, and leaves the F^- ion, the F^- becomes F^0, a V_k center, that is to say, the ESR signal of the V_k centers enhances as the temperature increasing, it shows annihilation of the Frenkel exciton and creation of the V_k center. Owing to the existence of the Frenkel excitons excited by γ-ray irradiation, the exciton is nonmagnetic, and it can not be detected with ESR, but can become a V_k center with heating. It is the reason why the ESR signal of the V_k center does not decline monotonously with the temperature increasing as those of the H, F and M centers do. The ESR signal of the V_k center enhances as the temperature increasing, it is a witness to annihilation of the Frenkel exciton. The difference of $BaCl_2$ from BaF_2 is that the attraction of the Cl atom to electron is more weaker than that of F atom, so Frenkel exciton can not form in $BaCl_2$.

The γ-ray irradiation induced the paramagnetic point defects V_k, H, F and M centers in the sample #1, and the V_k in the sample #2. Nonmagnetic Frenkel exciton can also be induced by the γ-ray irradiation at room temperature. It is noticed that annihilation of the Frenkel exciton emerges the V_k center, so one should pay much attention to the irradiated characteristic of BaF_2 crystallite powder in its application.

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