ESR Investigation on Natural Barite Samples Collected from Mangampeta Mines of Cuddapah District, Andhra Pradesh, India

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Abstract

Natural Barite was collected from Mangampeta mines of Cuddapah District, Andhra Pradesh, India, where it is one of the most common gangue minerals in the ore. The collected samples were subjected to ESR studies. The ESR spectrum of collected barite sample shows the existence of the hole type centre SO_4^- with the g-factor values 2.022 and 2.015 and the electron type centre SO_3^- with the g-factor values 2.0055, 2.0032 and 2.0021. In order to evaluate the barite as a ESR dosimeter material, it is very essential to study the power dependence, dose response and isothermal annealing. The obtained results reveal that the collected barite sample can be utilized as a ESR dosimeter for high doses measurement.

Keywords: Natural barite, ESR, High dose measurement, Dose response, Radicals identification

Introduction

Barite is becoming more important for the environmental applications (Jeffrey S. Hanor, 2000). It consists of divalent cation Ba^{2+} and a divalent tetrahedral molecular anion, SO_4^{2-} . It has an orthorhombic crystal form (Krystek, 1980). In the unit cell, the SO_4^{2-} and Ba^{2+} ions lie on the mirror planes and Ba^{2+} ions link the SO_4^{2-} ions in such a way that each Ba^{2+} ions coordinated by twelve oxygen (Deer et al., 1966). Studies by Melikove and Vukovic (1975) have shown the presence of barium and sulphate vacancies in the barium sulphate lattice. It is also observed that the concentration of these vacancies can be very high. Sulphoxy radicals like SO_2^-, SO_3^- and SO_4^- associate with barium vacancies. ESR was proposed several years ago as a method to measure radiation doses. Recently, most studies have been concerned with L-alanine. Crystalline alanine has excellent properties as regards tissue equivalence, linear dose-response and radical stability. ESR method still to be a realistic alternative to existing dosimetric system, e.g., ionization chambers, Si-diodes, thermoluminescence or chemical dosimetry [Lund et al., 2002].

ESR technique was used as a tool for implementing the information achievable by the thermoluminescence (TL) technique (Gundu Rao et al., 1996; Shinde et al., 1996; Madhusoodanan et al., 1999). According to Shinde et al., (1999) it was observed that the electron spin resonance (ESR) spectra of irradiated $BaSO_4$:Eu and $BaSO_4$:Eu,P prepared by the co-precipitation method, shows the presence of two distinct defect centres which were assigned to SO_2^- (A) and SO_2^- (B). Electron spin resonance investigation has shown that the defect centres which play a crucial role in TSL. Release of hole/electron from defect centres at the characteristic traps initiates luminescence processes in the material. The formation and stability of the defect centres depends on the crystal formation and impurity ion. In the present work, ESR investigation of collected barite sample was carried out in order to identify the defect centre present in the lattice and evaluate its use as a dosimeter (ESR) material.

Materials and method

In the present investigation, several well-grown black coloured barite crystals were collected from Mangampeta mines of Cuddapah District, Andhra Pradesh, India.Andhra Pradesh, India. About 10 samples were collected at different locations from the same rock bed. All these samples were crushed and ground carefully with a mortar and pestle and washed for 2 min with 1% HCl solution and finally with distilled water to remove any organic material and then dried in an oven. Grains sizes between 125 - 250µm in diameter were used for the measurements. Magnetic particles were removed using a magnet.

For electron spin resonance (ESR) measurements, samples were prepared following standard procedures and ESR spectra were recorded on a JEOL TES100 ESR spectrometer, having 100 kHz field modulation and phase sensitive detection. DPPH with a g value of 2.0036 was used as an internal standard for g factor calculations. The EPR defects, i.e., unpaired electrons are created in the samples by α-, β- or γ-rays. The concentration of the unpaired electrons can be determined directly by microwave absorption giving the EPR signal intensity. These unpaired electrons are trapped by an impurity or left at a hole, either of which is simply called "defects".

Results and Discussion

Electron Spin Resonance (ESR)

Figure 1(a) shows the ESR spectrum of natural barite sample (as such collected) which is having the g factor values of 2.022 and 2.015. Figure 1 (b) shows the ESR spectrum of irradiated barite sample (^{60}Co gamma-ray of a test dose of 100 Gy), which shows the triplet signal having the g factor values of 2.0055, 2.0032 and 2.0021. Further, the sample was annealed at 400°C for 1h and irradiated with the same dose of 100Gy and the ESR spectrum was recorded. This also gives same signals as that of irradiated sample but only change in its intensity is observed.

ESR study gives more detailed information about the nature of defect center exists in the materials, which plays a main role in the charge traps. ESR of irradiated solids is due to unpaired trapped charge carriers in the material, it could be surmised that the different traps are the basic nature of the host materials and the added dopants influence only the relative populations in the various traps. In fact the presence of isolated paramagnetic host lattice radicals like SO_4^- SO_3^- etc, in gamma-irradiated sulphate salts like K_2SO_4, Na_2SO_4, etc, almost independent of their environment in the crystal lattice has been verified by Atkins and Symons 1967. ESR powder patterns of gamma-irradiated sulphates of Ca, Sr and Ba at liquid-nitrogen temperature have been reported by Spitsyn et a1 (1964) and for $BaSO_4$ (with various impurities other than RE as dopants) by Gupta et a1 (1974) who identified the various peaks to host lattice radicals like SO_4^-, SO_3^-, O^-, etc produced by gamma irradiation. Krystak (1980) have identified the SO_4^- and SO_3^- radicals in barium sulphate lattice through ESR studies. He predicted the g-factor values for hole trapping center and electron trapping center as 2.0323, 2.0038, 2.0066 and 2.0001, 2.0032, 2.0032 respectively for the above mentioned radicals. Sharf and Hasian (2004) also studied the ESR characterization for barium sulphate samples. They reported a hole type and electron type center having the g factor values of 2.019, 2.0127, 2.0103 (SO_4^-) and 2.0039, 2.0028, 2.0001 (SO_3^-) respectively.

In the present study, the obtained g-factor values are compared with the available literature values, it can be concluded that the g values obtained from as such collected samples could be related to the hole-type defect center and it corresponds to SO_4^- radical and the g values obtained from the irradiated ESR spectrum reveals that it could be related to the electron type defect center and corresponds to SO_3^- radicals (Sharaf and Hassan, 2004; Krystek, 1980). The slight digression between the literature and observed g values may be due to the lattice environment of the radicals.

Power Dependence

In ESR measurement, an appropriate power setting is required since some of the ESR signal's intensity is saturated at low power setting but some of them increases with increase of power and attains a maximum intensity. Hence, an attempt made in this study and the microwave power dependence of ESR signal (electron center) of barite is shown in Figure 2. From this it is observed that the signal intensity increases as a function of power up to 2mW and decreases with further increase of microwave power.

Dose response

After irradiation, one new peak (g = 2.0055) is observed in the ESR studies (figure 1) it is due to radiation induced defect (electron type center SO_3^-). So this radiation induced peak can be utilized as dosimetric peak and the dose response future was analyzed. Hence, the linear response of the ESR signal to induced γ-irradiation was tested by irradiating the barite sample up to dose of 100 KGy and the ESR signal intensity was monitored and it shown in figure 3. From this, the observed relationship between γ-dose and the peak-to-peak height of the ESR signal shows a linear function in the dose range of 1–20000 Gy. After that, the signal gets saturated upto a given dose of 100 KGy.

Isothermal Annealing

This technique is used to determine the life time of the defects in the sample. For this study, the sample is irradiated with a dose of 1 KGy and heated from 20 to 300 °C, each step an increment of 20°C. Figure 4 shows the effect of isothermal heating on the ESR signal intensity of barite sample. From this it is observed that the relative intensity of the ESR signal decreases with increase of temperature. The intensity of ESR signal is decreased sequentially with temperature upto 140°C which shows a 15% reduction in its intensity. At 200 °C, 40 % of reduction in intensity is observed. A 90 % of intensity is reduced after reaching temperature of 220°C. Thus, it is observed that the stability of the traps is high enough below 140°C.

Conclusion

The ESR analysis of natural black coloured barite samples were collected from Mangampeta mines of Cuddapah District, Andhra Pradesh, India (as such) showed a signal of hole-type centre with g factor of 2.022 and 2.015. After irradiation (100 Gy) of the same sample of, an additional ESR signal is appeared, this is due to electron-type centre with having the g-factor values of 2.0055, 2.0032 and 2.0021. The hole type centre could be related to the SO_4^- radical and the electron - type centre could be related to SO_3^- radicals. The power dependence curve increases linearly upto 2 mW. The absorbed dose and the peak-to-peak height of the ESR first derivative line suggest a linear function in the dose range of 1–20000 Gy. From isothermal annealing, intensity of the ESR signal decreases sequentially with increase of temperature up to 140°C after that a deep decrease in intensity and reaches to zero at 240°C.

Figure 1- ESR Spectra for unirradiated (a) and gamma irradiated (b) barite.

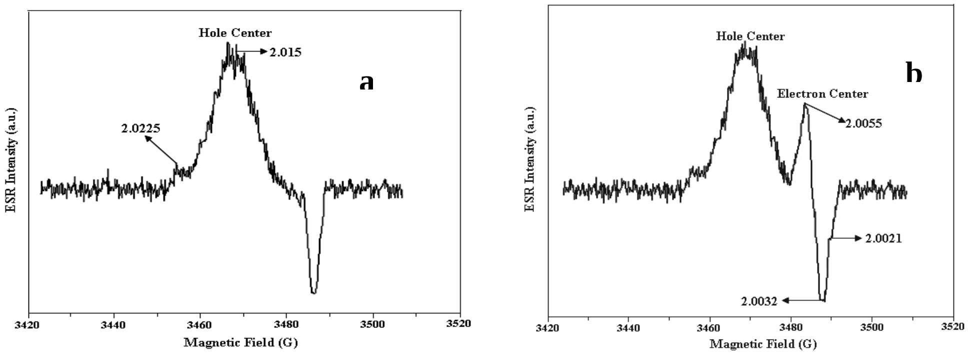


Figure 2- Shows the microwave power dependence of ESR signal of barite signal irradiated by gamma rays.

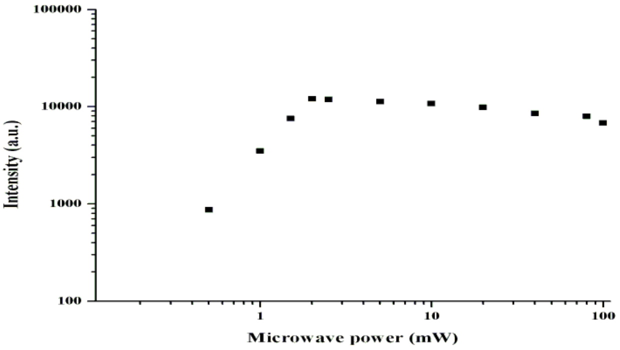


Figure 3 ESR response curve of the barite sample exposed to different doses of ^{60}Co gamma-rays.

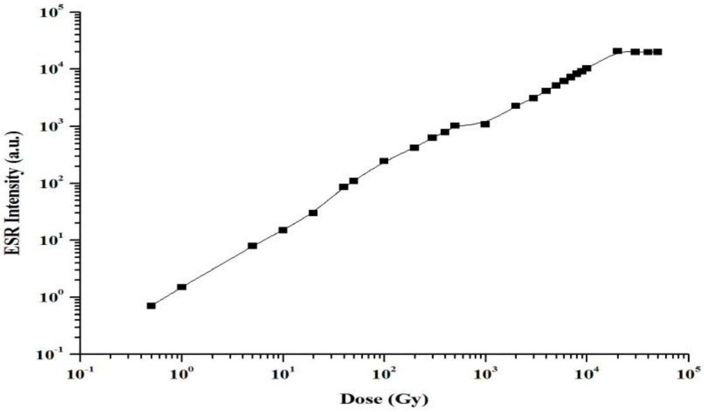
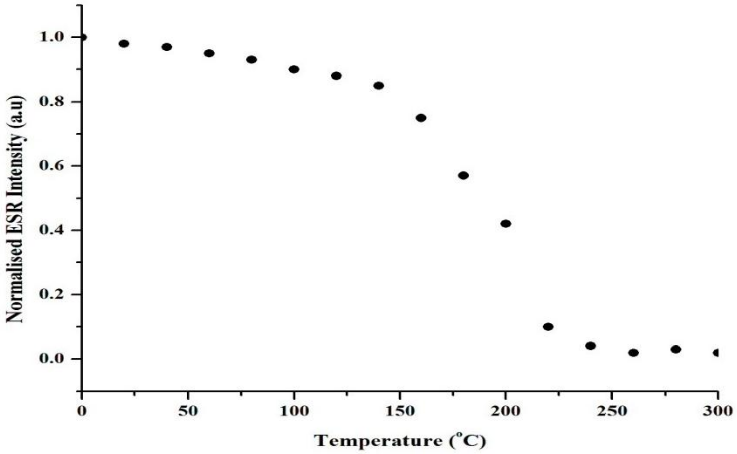


Figure 4 shows the Effect of isothermal annealing temperature of ESR signal.



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