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1991 J. Phys.: Condens. Matter 3 6909

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ESR of Fe-doped cristobalite AlPO_4

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Received 29 April 1991

Abstract. The ESR spectrum of iron-doped cristobalite AlPO_4 has been observed in the temperature range 25–250 °C. The spectrum, attributed to Fe^{3+} in a distorted tetrahedral site, changes very little in this temperature interval and can be described by a spin Hamiltonian of orthorhombic symmetry. The room-temperature Hamiltonian parameters are: $g = 2.000$, $|D| = 0.169 \text{ cm}^{-1}$ and $|E| = 0.005 \text{ cm}^{-1}$. The results suggest that, in contrast to that of Mn, the valence of the Fe ions is not affected by the α – β phase transition, which occurs at about 200 °C.

1. Introduction

Aluminium orthophosphate (AlPO_4) is a quartz analogue that exhibits structures similar to that of all SiO_2 polymorphs (Beck 1949). The cristobalite structure, in particular, is stable below 815 °C and undergoes a reversible α – β phase transformation (Leadbetter and Wright 1976) at about 200 °C. In this work, the ESR spectrum of Fe-doped AlPO_4 heat treated in two different atmospheres (air and argon) was investigated in the temperature range 25–250 °C, i.e. both above and below the α – β transition temperature.

2. Experimental procedure

The powder samples used in this study were prepared by reacting high-purity α - Al_2O_3 with H_3PO_4 at 320 °C for 1 h. The resulting precipitate was washed, dried and converted to cristobalite by firing at 1350 °C for 48 h. Appropriate amounts of Fe_2O_3 in powder form, up to 0.2 mol% Fe, were mixed with the precipitate before firing. Two different batches of samples were prepared: in the first, the firing step was performed in air; in the second, firing was performed in an argon atmosphere. Room-temperature x-ray diffraction patterns of all samples matched, within experimental error, the spectrum (Mooney 1956) of α -cristobalite AlPO_4 . No other phases were detected.

ESR measurements were performed at 9.5 GHz using a Varian E-12 ESR spectrometer. The quartz tube holding the samples was heated by hot dried air flowing through a solenoid valve which was operated by a temperature controller connected to a chromel–alumel thermocouple, in contact with the sample. No appreciable changes in the spectra were observed when the samples were held at the same temperature for several hours.

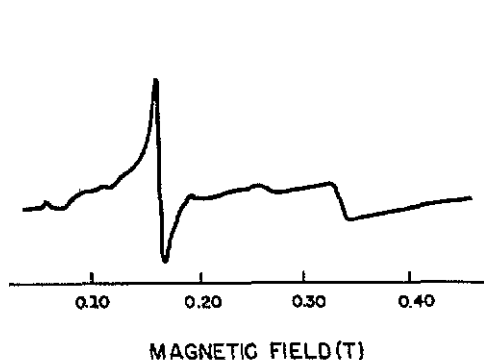


Figure 1. The X band ESR spectrum of cristobalite AlPO_4 doped with 0.2 mol % Fe, measured at 25 °C.

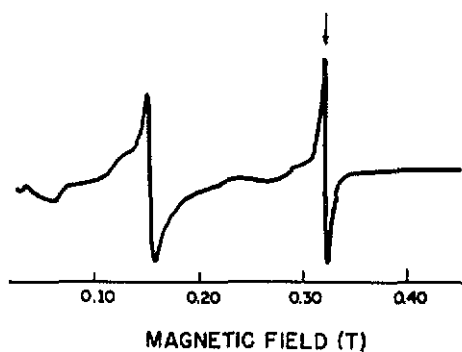


Figure 2. As figure 1, but measured at 200 °C.

3. Experimental results and analysis

The ESR spectra of samples fired in air and in argon are indistinguishable. A typical room-temperature spectrum is shown in figure 1. It can be interpreted with the help of the spin Hamiltonian

$$\mathcal{H} = g\beta H \cdot S + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 + S_y^2) \quad (1)$$

with $S = 5/2$.

Approximate values of D and E in equation (1) were determined using the plots given by Barry (1967). The Hamiltonian (1) was then diagonalized along the principal axes and the parameters g , D and E were adjusted for the best fit with experiment. The final results were:

$$g = 2.000 \pm 0.005 \quad |D| = 0.169 \pm 0.001 \text{ cm}^{-1} \quad |E| = 0.005 \pm 0.001 \text{ cm}^{-1}.$$

The values of the spin-Hamiltonian parameters g , D and E given above are close to the values reported for the isoelectronic Mn^{2+} ion in the same host lattice (de Biasi and Simões 1989) and are consistent with an Fe^{3+} centre in a distorted tetrahedral site (Wertz and Bolton 1972).

The spectrum changes very little when the temperature is increased above room temperature. The only new feature is a narrow line (indicated by an arrow in figure 2) that is seen above 175 °C at a field of approximately 0.32 T. The same line was observed by de Biasi and Simões (1987) in undoped samples of cristobalite AlPO_4 and attributed to a paramagnetic defect in the β -phase.

4. Discussion

The fact that the spectrum of Fe-doped AlPO_4 is the same in samples prepared in argon and in air and changes very little when the temperature is increased above the α - β transition temperature suggests that the Fe^{3+} ion is very stable in this compound. In particular, the valence changes observed for the isoelectronic ion Mn^{2+} (de Biasi and Simões 1989) near the α - β transition are completely absent in the case of Fe^{3+} .

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