

ESR in Mn-doped cristobalite AlPO_4

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 5915

(<http://iopscience.iop.org/0953-8984/1/34/009>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:41

Please note that [terms and conditions apply](#).

ESR in Mn-doped cristobalite AlPO_4

R S de Biasi and A Simões

Centro de Pesquisa de Materiais, Instituto Militar de Engenharia, 22290 Rio de Janeiro, RJ, Brazil

Received 14 March 1989, in final form 3 May 1989

Abstract. ESR spectra are reported for powder samples of Mn-doped cristobalite AlPO_4 heat treated in two different atmospheres: argon and air. The spectra are attributed to Mn^{2+} and Mn^{4+} ions, respectively. The temperature dependence of the spectrum intensities suggests that the Mn ions undergo a valence change that occurs in the same temperature range as the α - β phase transition.

1. Introduction

Aluminium orthophosphate (AlPO_4) is a quartz analogue that exhibits structures similar to those 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 Mn-doped cristobalite 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 MnO_2 in powder form, up to 0.4 mol% Mn, 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 operated by a temperature controller connected to a chromel–alumel thermocouple in contact with the sample. Line parameters were measured after each sample was kept for at least 1 min at a given temperature. No appreciable changes in line parameters were observed when the samples were held at the same temperature for longer times, up to 1 h.

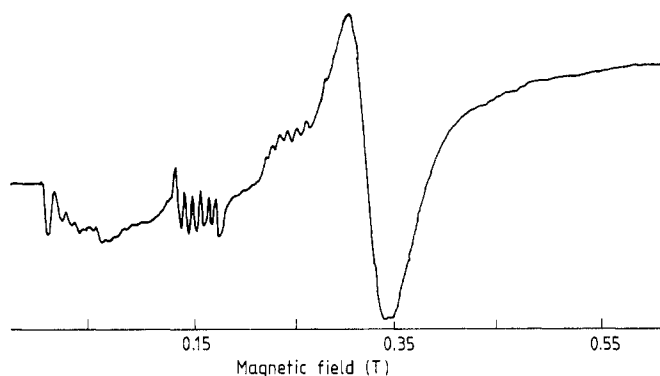


Figure 1. The X-band ESR spectrum of cristobalite AlPO_4 doped with 0.2 mol% Mn and fired in argon, measured at 25 °C.

3. Experimental results

3.1. Samples fired in argon

The room-temperature ESR spectra of samples fired in argon show several hyperfine multiplets (see figure 1). When the sample temperature is increased above room temperature, the intensity of these multiplets decreases slowly in the temperature interval 25–150 °C and then much faster in the range 150–200 °C (figures 2 and 3). The spectra also show a single intense line with $g \approx 2$ whose intensity remains practically unchanged in the temperature interval 25–200 °C. Above 200 °C and up to 250 °C, no further changes in the spectrum are observed.

The spectrum associated with the multiplets can be interpreted with the help of the spin Hamiltonian

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

with $S = \frac{5}{2}$, $I = \frac{5}{2}$.

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

$$\begin{aligned} g &= 2.000 \pm 0.005 & |E| &= 0.005 \pm 0.001 \text{ cm}^{-1} \\ |D| &= 0.163 \pm 0.001 \text{ cm}^{-1} & |A| &= (77.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}. \end{aligned}$$

The values of the spin-Hamiltonian parameters g , D and E given above are consistent with a Mn^{2+} centre in a distorted tetrahedral site (Wertz and Bolton 1972); the value of the hyperfine splitting parameter A is of the same order as for the Mn^{2+} ion in other host lattices (Orton 1969, Goodman and Raynor 1970).

3.2. Samples fired in air

The room-temperature spectra of samples fired in air show only a broad, almost symmetric line (see figure 4). When the sample temperature is increased above room temperature, a multiplet appears at about 150 °C (see figure 5). The line amplitude of

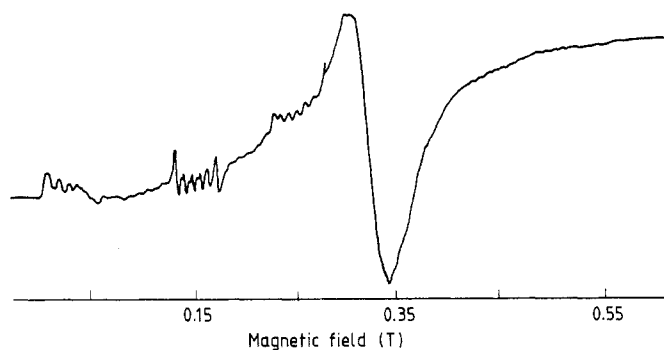


Figure 2. As figure 1, but measured after the temperature was increased to 150 °C.

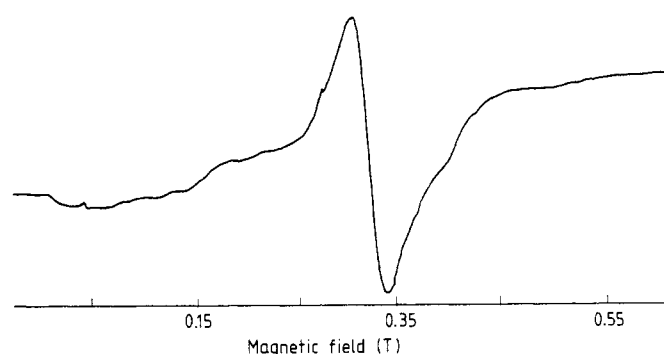


Figure 3. As figure 1, but measured after the temperature was increased to 200 °C.

the multiplet increases rapidly with increasing temperature up to about 200 °C (see figure 6) and remains constant for higher temperatures. The intensity of the multiplet lines shows hysteresis behaviour; the hysteresis loop, obtained by measuring the line intensity at 10 °C intervals as the temperature was changed from 140 to 250 °C and back to 140 °C, is shown in figure 7. It is similar to the curve that shows the fraction of the β -phase, as determined by x-ray diffraction, as a function of temperature (figure 6 of Leadbetter and Wright 1976).

The spectrum associated with the multiplet can be interpreted with the help of the spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + AS \cdot \mathbf{I} \quad (2)$$

with $S = \frac{3}{2}$, $I = \frac{5}{2}$.

Up to second order in $A/g\beta$, the resonance fields for the $\frac{1}{2}$, $m \rightarrow -\frac{1}{2}$, m transitions are given by (Van Wieringen and Rensen 1963)

$$H_m = H_0 - (A/g\beta)m - (1/2H_0)(A/g\beta)^2(\frac{35}{4} - m^2) \quad (3)$$

where $H_0 = h\nu/g\beta$ and $-\frac{5}{2} \leq m \leq \frac{5}{2}$.

A fitting of equation (3) to the experimental results at 200 °C yielded the following results:

$$g = 1.999 \pm 0.0005 \quad |A| = (82.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}.$$

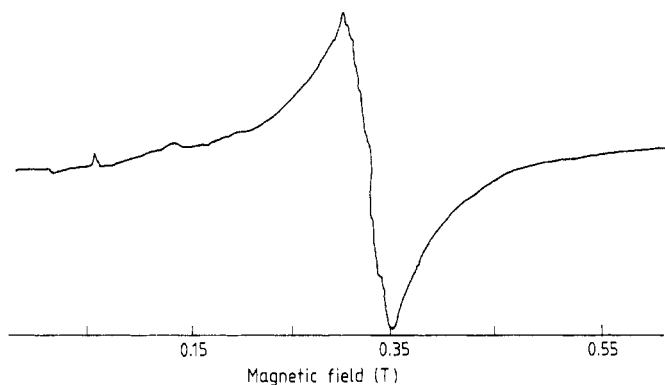


Figure 4. The X-band ESR spectrum of cristobalite AlPO_4 doped with 0.2 mol% Mn and fired in air, measured at 25 °C.

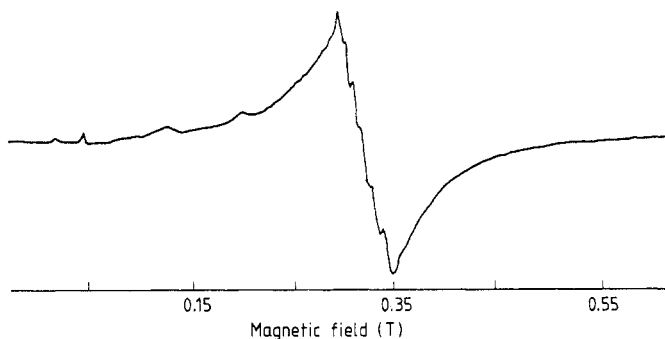


Figure 5. As figure 4, but measured after the temperature was increased to 150 °C.

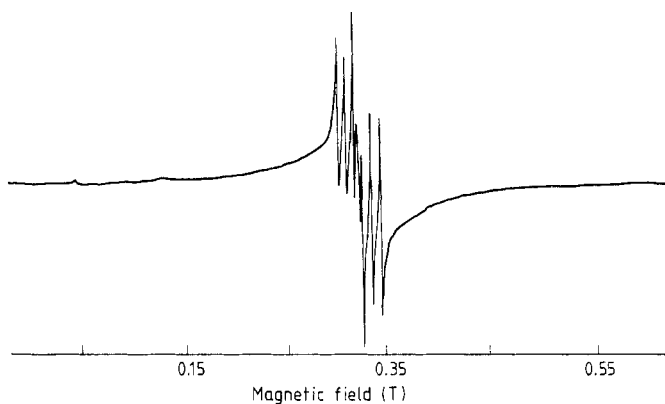


Figure 6. As figure 4, but measured after the temperature was increased to 200 °C.

The values of the spin-Hamiltonian parameters g and A above are consistent with a Mn^{4+} centre in a tetrahedral site (Wertz and Bolton 1972); they are of the same order as for the Mn^{4+} ion in other host lattices (Henderson and Hall 1967, Orton 1969, Goodman and Raynor 1970).

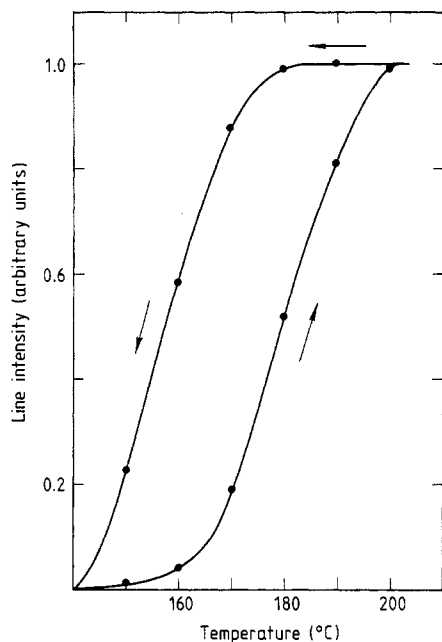


Figure 7. The intensity of the ESR spectrum of Mn^{4+} in cristobalite AlPO_4 , showing hysteresis behaviour.

4. Discussion

According to the experimental results, the spectrum of the Mn^{2+} ions is seen only in the α -phase of cristobalite AlPO_4 , while the spectrum of the Mn^{4+} ion is observed only in the β -phase. A plausible explanation for this seems to be a valence change associated with the α - β phase transition. Let us assume that the manganese ions in the α -phase are present as Mn^{2+} in samples fired in an argon atmosphere and as Mn^{3+} in samples fired in air. If the manganese ions lose one electron in the α - β transformation, these ions become Mn^{3+} and Mn^{4+} , respectively, in the β -phase. Since Mn^{3+} is a $3d^4$ ion, whose spectrum is seldom observed at room temperature or above due to short spin-lattice relaxation times (Orton 1969, Goodman and Raynor 1970), the only observable spectra would be those due to Mn^{2+} in the α -phase of samples fired in argon and to Mn^{4+} in the β -phase of samples fired in air. A similar charge transfer has been observed in berlinite AlPO_4 (Scott 1971), where the nominal valences of Al and P ions, as measured using the Raman effect, are approximately +4 instead of +5 and +3, as usual. If the same phenomenon occurs in undoped β -cristobalite AlPO_4 , it could be responsible for the appearance of an ESR line that is seen only in the β -phase (de Biasi and Simões 1987).

As to the broad, symmetric, temperature-independent line that is observed for all samples, it is certainly associated with the manganese ions, because it is not observed in undoped samples (de Biasi and Simões 1987); it is probably due to Mn clusters. In fact, a similar curve has been observed for Mn-doped MgO (Gesmundo and Rossi 1973).

References

- Barry T I 1967 *NPL Report IMU Ex6*
 Beck W R 1949 *J. Am. Ceram. Soc.* **32** 147
 de Biasi R S and Simões A 1987 *J. Phys. C: Solid State Phys.* **20** 5573

- Gesmundo F and Rossi P F 1973 *J. Solid State Chem.* **8** 297
- Goodman B A and Raynor J B 1970 *Electron Spin Resonance of Transition Metal Complexes* (New York: Academic) ch VIII
- Henderson B and Hall T P P 1967 *Proc. Phys. Soc.* **90** 511
- Leadbetter A J and Wright A F 1976 *Phil. Mag.* **33** 105
- Mooney R C L 1956 *Acta Crystallogr.* **9** 728
- Orton J W 1969 *Electron Paramagnetic Resonance* (New York: Gordon and Breach) ch 11
- Scott J F 1971 *Phys. Rev. B* **4** 1360
- Van Wieringen J S and Rensen J G 1963 *Paramagnetic Resonance* vol 1, ed. W Low (New York: Academic) p 105
- Wertz J E and Bolton J R 1972 *Electron Spin Resonance* (New York: McGraw-Hill) ch 11