LOCALIZATION OF CO$_3^-$ ANION RADICALS IN STRONTIUM CARBONATE OBTAINED BY THERMAL DECOMPOSITION OF STRONTIUM OXALATE

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Abstract—Mn$^{2+}$ EPR probes and transmission electron microscopy are used to study the influence of the thermal decomposition rate of strontium oxalate monohydrate on the morphology and the extended defects in the SrCO$_3$ formed. The correlations between relevant EPR parameters of Mn$^{2+}$-probes and CO$_3^-$ radicals trapped in the product indicate localization of both species in the vicinity of extended defects such as stacking faults, dislocations and grain boundaries.

Keywords: CO$_3^-$ anion radical, strontium carbonate, extended defects, Mn$^{2+}$ EPR probe, strontium oxalate thermal decomposition.

1. INTRODUCTION

Stabilization of equal amounts (about $10^{-6}$mol) of two kinds (A and B) of CO$_3^-$ anion radicals was established by EPR in strontium carbonate (aragonite-type crystal structure) obtained by thermal decomposition of strontium oxalate whereas such species were not observed in strontium carbonate prepared by precipitation with CO$_2$ [1]. This finding was interpreted as an indication in favour of the mechanism of oxalate salt decomposition proposed by Boldyrev et al. [2], according to which CO$_3^-$ anion radicals represent intermediates in the transformation of the oxalate ions (C$_2$O$_4^{2-}$) into carbonate (CO$_3^{2-}$):

$$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_3^{2-} \rightarrow \text{CO}_3^{2-} + \text{CO}_2^+.$$ 

It has also been found [3] that admixed Li$^+$ ions react selectively with the radicals transforming CO$_3^-$-A into CO$_3^-$-B thus permitting identification of the former as luminescence centres in SrCO$_3$. However, there are still not sufficient data on the manner in which they react and the site of stabilization of these defects in the crystal lattice of strontium carbonate. On the basis of the different spin-lattice relaxation times of the two kinds of radicals it has been suggested that they should be in different environments in the crystal lattice, e.g. site-localized (CO$_3^-$-A) and interstitial (CO$_3^-$-B) [1]. However, a more detailed analysis of this suggestion gives rise to a series of difficult questions. For instance, annealing of the strontium carbonate obtained leads to a drop in concentration of the two radicals ([CO$_3^-$-A] = [CO$_3^-$-B]) according to a second order rate kinetic equation [1]. This could be the case if the bulk of the aragonite crystal lattice ensures a high mobility of the radicals and there is an equal probability for every CO$_3^-$-A species to react with any CO$_3^-$-B one, which could hardly be accepted. In addition, lithium doping of the bulk of the aragonite crystal lattice should hardly allow an easy interaction of the Li$^+$ ions with the CO$_3^-$ anion radicals, if they were stabilized there [3]. On the other hand, the site of stabilization of the radicals has to depend not only on the mechanism of their formation but also on the intrinsic defects in the SrCO$_3$ matrix, i.e. on extended defects such as dislocations, stacking faults, twinning planes, small-angle grain boundaries, etc. In this paper, extrinsic EPR probes and transmission electron microscopy (TEM) are used to investigate the changes in the structure of the strontium carbonate matrix depending on the rate of thermal decomposition of strontium oxalate with a view to finding correlations with the amounts of stabilized CO$_3^-$ radicals, which would permit conclusions concerning the radical localization. The extrinsic EPR probes used were admixed Mn$^{2+}$ ions.

2. EXPERIMENTAL

The preparation of pure SrC$_2$O$_4$·H$_2$O samples is described in Ref. 1. Mn$^{2+}$-doping of the SrC$_2$O$_4$·H$_2$O samples was achieved by precipitation from a solution of Sr$^{2+}$ and Mn$^{2+}$ ions (0.4 mol %) with an ammonium oxalate solution at pH = 5. The precipitate obtained was washed with water and dried at 100–120°C. Some of the SrC$_2$O$_4$·H$_2$O samples were ground in a Retsch friction grinder for 6 h. The samples of SrC$_2$O$_4$·H$_2$O and SrC$_2$O$_4$·H$_2$O·Mn$^{2+}$ were heated in a nitrogen flow up to the decomposition temperatures (490 and 530°C) with rates of
5 and 60 min−1, respectively. For the sake of convenience, these samples will be denoted by SrCO3-5, SrCO3-60, SrCO3-Mn-5 and SrCO3-Mn-60, respectively. At the final decomposition temperatures (490 and 530°C), the samples were heated for 10–60 min. These decomposition temperatures were chosen so as to obtain an aragonite-type strontium carbonate (according to X-ray and IR analyses) and maximum initial concentrations of the CO2 radicals. Reference samples of SrCO3-Mn2+ obtained with a decomposition rate of 60 min−1 were also ground for 6 h.

The samples of SrCO3-Mn2+ obtained from SrC2O4·H2O·Mn2+ at a decomposition rate of 5 min−1 were heated at 530, 750 and 900°C for 6 h and cooled slowly (with a rate of about 5 min−1) to room temperature in order to carry out control measurements.

TG and DTG studies were performed with an STA 780 (Stanton Redcroft Ltd, England) apparatus in the range 20–700°C at a rate of 5 and 50 min−1. A platinum crucible, 6 mm in diameter, and a sample weight of ca 19 mg were used. The specific surface area of the samples was determined by the Klyachko-Gurvich method [4].

TEM studies were carried out with a Philips TEM 420 transmission electron microscope using a 100 kV accelerating voltage. The EPR-spectra were recorded at room temperature as first derivatives of the absorption signal in the X- and Q-bands (ν = 9.4 and 34.5 GHz, respectively) of an ERS 220/Q spectrometer produced in the Academy of Sciences of the G.D.R. The g-values and the concentration of paramagnetic centres were determined with respect to Mn2+/ZnS standard samples.

3. RESULTS

Figure 1 presents the DTG curves of dehydration of SrC2O4·H2O to SrC2O4 and thermal decomposition of SrC2O4 to SrCO3 with a heating rate of 5 (1) and 50 min−1 (2). In contrast to the DTG curves of dehydration, the DTG curves of thermal decomposition have different shapes at the two different heating rates. At 50 min−1 the DTG peak in the range 430–530°C may be decomposed into at least two components while at the slow decomposition there is only one single peak. For the sake of comparison, the same figure shows the change in specific surface area of the samples during dehydration and thermal decomposition depending on the heating rate. Obviously, the specific surface area of the samples strongly increases, but its value is independent of the heating rate within the experimental error. The mean size of the crystallites as determined from the specific surface area (r = 6/pδ, where p is the density) is about 150 nm and is in good agreement with the crystallite sizes (50–200 nm) established by TEM. Depending on the heating rate, aggregates of microcrystals differing in shape and size are formed. Prismatic aggregates [500 and 3000 nm, Fig. 2(A)] prevail in SrCO3-5, while isometric aggregates [up to 500 nm, Fig. 2(B)] are predominant in SrCO3-60. Figure 3 shows light and dark field images of some sufficiently thin crystals of strontium carbonate obtained with a decomposition rate of 60 min−1. Evidently, there are extended defects in the crystallites such as dislocations, stacking faults, twins, etc. Owing to the small crystal sizes, it is difficult to determine exactly the kind of defects. With rising temperature of heat-treatment of the strontium carbonate, the microcrystals recrystallize (size of about 500 nm) and exhibit no defects [Fig. 3(B)].

In the X-band, SrC2O4·H2O coprecipitated with Mn2+ ions has the characteristic six-line EPR spectrum of electronic transition (m = 5/2, 3/2, 1/2, −1/2, −3/2 and −5/2 is the nuclear magnetic quantum number) with g = 2.002 and A = 96 Oe (ΔM = 0) and five pairs of “forbidden” lines (ΔM = 1) between them. Here g is the g-factor of the unpaired electrons, A is the hyperfine-interaction constant and M is the electron magnetic quantum number. In addition, the lines of both allowed and forbidden transitions are split. Within the framework of the perturbation theory, the splitting (Δ) of the lines and relative intensity (J//J) of the forbidden transitions is given by the expressions [5]:

\[ \Delta = \frac{(50/9)\gamma^2(\nu/g\beta H)^2}{1 - 2\gamma M \mu B \mu H} \]

\[ J//J = \frac{3D}{4g\beta H} \sin^2\theta \left(1 + \frac{5(S^* + 1)}{3M(M - 1)}\right)^3 \times \{4I(I + 1) - m^2 - m\}, \]
where $S$ and $I$ stand for electron and nuclear spins of the $\text{Mn}^{2+}$ ions, respectively ($\beta$ is the Bohr magneton, $H$ is the external magnetic field and $\theta$ is the angle between the axis of the local crystal field and the external magnetic field). On the basis of these expressions, the fine structure constant $D$ can be estimated: $D \approx 70 \text{ Oe}$. It represents the splitting of the spin multiplet in the crystal field of axial symmetry when $H = 0$. The amount of $\text{Mn}^{2+}$ ions observed by EPR is about $10^{-4} \text{ mol\%}$. In the Q-band, the intensity of the forbidden lines decreases, and these six allowed lines are singlets with a Lorentzian shape and a mean width of 8 Oe.

During dehydration followed by thermal decomposition, the EPR spectrum of the $\text{Mn}^{2+}$ ions shows only small quantitative changes. Irrespective of the heating rate during the dehydration of strontium oxalate monohydrate, the constants of the hyperfine
Fig. 3. Light and dark field images of microcrystals of SrCO$_3$-60 heated at 530°C (A) and SrCO$_3$ heated at 750°C (B) for 6 h.

(A) and fine (D) structures, the mean line-width ($\Delta H_p$: Q-band) and the relative amount of the Mn$^{2+}$ ions increase slightly (Fig. 4). At the next step of thermal decomposition of the anhydrous strontium oxalate there is a small drop in the values of all these quantities. Depending on the thermal decomposition rate, the decrease in the D, A and $\Delta H_p$ values is different: it is more pronounced for the SrCO$_3$-5 sample. Simultaneously, the line shapes of the allowed transitions change. They are inhomogeneously broadened, especially for the SrCO$_3$-Mn-60 sample. In addition, the amount of Mn$^{2+}$ ions observed by EPR decreases about 5 times in comparison with the amount in the initial strontium oxalate monohydrate, this decrease being more pronounced with SrCO$_3$-Mn-3.

Under isochronous conditions (6 h), the amount of Mn$^{2+}$ ions observed by EPR obviously drops with rising temperature of heating of the SrCO$_3$ obtained, the fine and hyperfine structure constants and the mean width of the signal (in the Q-band) remaining unchanged. At about 900°C, no sextet of isolated
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Fig. 4. Changes in values of the hyperfine structure constant, $A$, fine structure constant, $D$, mean signal width $\Delta H_{pp}$ in the Q-band and relative amount, $r$, of the Mn$^{2+}$ ions (II) during dehydration and thermal decomposition of SrC$_2$O$_2$·H$_2$O at heating rates of 5° min$^{-1}$ (curve 1) and 60° min$^{-1}$ (curve 2).

Fig. 5. Dependence of the mean line-width ($\Delta H_{pp}$) of the Mn$^{2+}$ ions (I) and the concentration of the CO$_2^-$ anion radicals (II) on the annealing time of SrCO$_3$ obtained at decomposition rates of 5° min$^{-1}$ (curve 1) and 60° min$^{-1}$ (curve 2).

Mn$^{2+}$ ions are seen: there is a singlet with a width of about 350 Oe. Within the same temperature range, the specific surface area of SrCO$_3$ strongly decreases from 7 m$^2$ g$^{-1}$ for SrCO$_3$·Mn heated at 350°C to less than 1 m$^2$ g$^{-1}$ for SrCO$_3$·Mn heated at 900°C.

Figure 5 shows the change in the signal mean width (in the Q-band) of the Mn$^{2+}$ ions in strontium carbonate prepared at a decomposition rate of 5 and 60° min$^{-1}$ depending on the heating time under isothermal conditions (490 and 530°C, respectively). With sample SrCO$_3$·Mn-60, the mean line-width ($\Delta H_{pp}$) decreases with annealing time, while the linewidth of the Mn$^{2+}$ ions for sample SrCO$_3$·Mn-5 displays no alteration. In addition, after 50 min of annealing the mean signal width for Mn$^{2+}$ ions is the same for the two samples (SrCO$_3$·Mn-5 and SrCO$_3$·Mn-60).

Figure 5 also shows the dependence, on the annealing time under isothermal conditions (490 and 530°C), of the concentrations of both kinds of CO$_2^-$ anion radicals (as mentioned in the Introduction, [CO$_2^-A$] = [CO$_2^-B$], [I]) in SrCO$_3$ obtained at decomposition rates of 5° and 60° min$^{-1}$. In SrCO$_3$·5, the concentration of CO$_2^-$ anion radicals is low and is independent of the annealing time, while in SrCO$_3$·60 the concentration of CO$_2^-$ in the initial moment is about 10 times higher and decreases during the annealing according to a second order rate equation: $1/N = 1/N_0 + k_t$ (1). When the thermal decomposition proceeds under nitrogen, carbon particles (identified according to the EPR signal C, Ref. 1) are deposited on the SrCO$_3$ surface due to disproportionation of the evolving carbon monoxide: 2CO $\rightarrow$ C + CO$_2$. In contrast to the concentration of CO$_2^-$ anion radicals, the amount of deposited carbon does not depend on the heating rate.

When SrC$_2$O$_4$·H$_2$O is ground in a friction grinder, its specific surface area increases threefold. However, the strontium carbonate obtained from this initial sample has the same specific surface area as does strontium carbonate prepared from strontium oxalate not subjected to mechanical treatment. In strontium carbonate from mechanically treated strontium oxalate monohydrate, about a threefold amount of CO$_2^-$ anion radicals are stabilized at the initial moment, but they disappear much more rapidly with annealing. The carbon amount on the surface (estimated from the intensity of the corresponding
EPR signal) of the two kinds of samples is the same.

4. DISCUSSION

In the EPR spectrum of the Mn$^{2+}$ ions, the parameter which is most sensitive to changes in symmetry of the crystal field is the fine structure constant ($D$). As mentioned above, this constant presents the splitting of the ground spin state of the Mn$^{2+}$ ions ($S = 5/2$) under the effect of an axial component of the crystal field. In the two polymorphic modifications (calcite and aragonite) of CaCO$_3$, the coordination polyhedra of the cations have different symmetries: $D_{4d}$ (calcite type) and $C_{3v}$ (aragonite type), while the coordination number of the cation (with respect to the oxygen particles in the carbonate ions) has values of six and nine, respectively. It is known that after isomorphic substitution of Mn$^{2+}$ for Ca$^{2+}$ ions in calcite and aragonite minerals, this difference in the local symmetries of the crystal field is displayed by the EPR spectrum of Mn$^{2+}$ as a strong increase in the fine structure constant: $D = 80$ cm$^{-1}$ for CaCO$_3$-Mn (calcite, Refs 6 and 7) and $D \approx 250$ cm$^{-1}$ (aragonite, Refs 8 and 9). It is clear that the fine structure constant of the Mn$^{2+}$ ions in our strontium carbonate matrix is close to the constant characteristic of Mn$^{2+}$ situated in a site of a calcite crystal lattice. In other words, the Mn$^{2+}$ ions observed by EPR ($10^{-4}$-$10^{-5}$ mol%) in SrCO$_3$ are situated in crystal fields with axial symmetry and have the coordination number six. In the bulk of the aragonite-type crystal structure this is impossible, hence extended defects should be considered as localization sites for the Mn$^{2+}$ ions. In the simplest case these can be stacking faults. Thus, the slipping of the $B$ layer of metal ions in the $(310)$ direction changes the $ABAB \cdots$ sequence of layers which is characteristic of the aragonite-type crystal structure, to an $ABC \cdots$ order which corresponds to a calcite-type crystal structure (Fig. 6, Ref. 10). The isolated Mn$^{2+}$ ions may also decorate dislocations and/or grain boundaries. As to the twinning planes, it is known that only the $(110)$ plane in the aragonite-type structure lattice can play such a role. According to the analysis of Wooster [11], the environment of the ions in this plane does not change, due to which the isolated Mn$^{2+}$ ions observed by EPR cannot be in these planes.

The possibility for Mn$^{2+}$ ions to be stabilized by appropriate extended defects is also in agreement with the change in the EPR spectrum of the Mn$^{2+}$ ions in the case of mechanical treatment of the SrCO$_3$ obtained, i.e. when additional defects are created. Besides, the Mn$^{2+}$ ions would prefer, due to their smaller ion radius, to be localized in those defects of the aragonite-type crystal structure where the coordination number is lower than nine. With increasing temperature of the strontium carbonate to above 500°C, the amount of isolated Mn$^{2+}$ ions strongly decreases due to the recrystallization and the resulting annihilation of crystal lattice defects (Fig. 3(B)).

The negligible change in fine and hyperfine structure constants (Fig. 4) of the Mn$^{2+}$ ions during the transformation of the SrC$_2$O$_4$:H$_2$O crystal lattice to that of SrCO$_3$ leads to the conclusion that the symmetry of the crystal field (where the Mn$^{2+}$ ions are situated) and the character of the chemical bond (Mn-O) undergo no substantial change. This means that in both the initial compound SrC$_2$O$_4$:H$_2$O and the product SrCO$_3$, the Mn$^{2+}$ ions come into crystal fields with axial symmetry and have the coordination number six. SrC$_2$O$_4$:H$_2$O [12] and CaC$_2$O$_4$:H$_2$O (whewelite type, Ref. 13) are isostructural. The coordination number of the metal ion in them (with respect to the oxygen particles in C$_2$O$_4^{2-}$ and H$_2$O) is six, but the symmetry of the coordination polyhedron is lower than $D_{4d}$. This is an indication that in both SrCO$_3$ and SrC$_2$O$_4$:H$_2$O, the Mn$^{2+}$ ions are not in the bulk of the crystal lattice. This is not unexpected in view of the Mn$^{2+}$-doping method. The different solubility of strontium and manganese oxalates and the different ionic radii of Sr$^{2+}$ and Mn$^{2+}$ are the reasons why only a small part (about $10^{-4}$ mol%) of the preset 0.4 mol% Mn$^{2+}$ are incorporated into defect sites of the SrC$_2$O$_4$:H$_2$O crystal matrix, while the remaining part of the ions are precipitated as a separate phase during the precipitation process. There is a similar situation during the precipitation of SrC$_2$O$_4$:H$_2$O in the presence of Li$^+$ ions, when lithium oxalate is adsorbed on the strontium oxalate species [3]. The question arose why during the thermal decomposition of this oxalate mixture, the Li$^+$ ions relatively quickly penetrated (at isothermal heating at 530°C) into the strontium carbonate matrix. This fact can now be explained by faster diffusion of Li$^+$ ions in the extended defects of the
SrCO₃. The penetration of the Li⁺ ions into SrCO₃ has been established on the basis of their effect on the EPR spectrum and the luminescence of the CO₂⁻ anion radicals [3]. Hence, it is not only the Li⁺ ions but also the CO₂⁻ anion radicals that occupy extended defects of the crystal matrix. In other words, the doped (Mn²⁺ and Li⁺) ions and the intrinsic defects (CO₂⁻ anion radicals) are stabilized in collective lattice defects of the strontium carbonate, e.g. stacking faults, dislocations, grain boundaries, etc.

Depending on the thermal decomposition rate, the kinetics of the solid state reaction as illustrated by the DTG curve shape [Fig. 1(I)], and the morphology of the SrCO₃ particles (Fig. 2) change. This leads to different distributions of the doped ions over sites with different local crystal fields. Then the Mn²⁺ ions which decorate the extended defects of the crystal matrix are characterized by a set of fine structure-constant and g-factor values, which is responsible for the inhomogeneous broadening of the lines of the EPR spectrum. When \( D \ll g\beta H \), these lines are singlets and their width reflects the distribution of Mn²⁺ ions in crystal fields close in symmetry but with varying strengths. The similar decreases in the line-width of the Mn²⁺ ions in doped SrCO₃ [Fig. 5(I)] and the concentration of CO₂⁻ anion radicals in pure SrCO₃ during annealing [Fig. 5(II)] indicate that the stabilization of the CO₂⁻ radicals depends on the disorder in the extended defect arrays. The higher the rate of thermal decomposition, the wider the distribution range of the particles in the extended defects with respect to bond lengths and bond angles and the larger the amount of CO₂⁻ radicals stabilized. With advancing heating, the distribution curve of the local fields becomes narrower, which is accompanied by a concentration drop of the CO₂⁻ anion radicals. The CO₂⁻ concentration also depends on the defects in the crystal lattice of the initial oxalate salt (the influence of the mechanical pretreatment mentioned above).

5. CONCLUSION

The present investigation shows that the CO₂⁻ anion radicals are stabilized in strontium carbonate around extended crystal lattice defects such as stacking faults, dislocations, grain boundaries, etc.

REFERENCES