

Electrical conductivity studies of cobalt-precipitation in RbCl crystals

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Abstract. The results of electrical conductivity measurements in heavily doped RbCl:CoCl₂ crystals with 2500 and 6000 ppm of cobalt are being reported in this paper. The different regions of the conductivity plots for the crystals with the two concentrations of cobalt have been explained and relevant energy parameters determined. The crystals with 6000 ppm of cobalt have been found to contain two types of precipitates one of these being of the same type as that existing in RbCl crystals with 2500 ppm of cobalt while the other being of a different composition.

Further, it has been found that the crystals appear blackened after heating during measurements. The blackening has been attributed to the expulsion of cobalt from the bulk of the crystal which forms an oxide at the surface.

Keywords. Electrical conductivity; expulsion; RbCl: CoCl₂; precipitation.

1. Introduction

Precipitation of divalent metal ion impurities in alkali halide crystals has been reported by a number of workers using different techniques. A comprehensive review of this subject has been given by Hartmanova (1971). Precipitation is a process which involves creation of a secondary phase: either a divalent metal halide or a chemical compound. This process is different from what is usually called an aggregation involving formation of dimers, trimers, pentamers etc.

The precipitates reported in the literature have distinct structural compositions in different cases *viz.*,

- (i) Precipitates with the structure 6MX.NX₂ where M represents an alkali ion, X a halogen ion, and N a divalent cation. Such a phase is known as Suzuki phase (Suzuki 1961), involving slight displacement of anions from their normal positions and has been found in systems such as NaCl:CdCl₂ (Suzuki 1961), LiF:MgF₂ (Lilley and Newkirk 1967), LiF:ZnF₂ (Sors 1973), NaCl:MnCl₂ (Chapman and Lilley 1975) and NaCl:MgCl₂ (Al-Jammal 1976).
- (ii) The precipitates of the type NX₂ (dopant) in systems such as NaCl:BaCl₂ (Hensel and Ziller 1968; Swamy Rao and Parasnis 1969, 1978) and NaCl:SrCl₂ (Laredo and Dartyge 1971).
- (iii) The precipitates of the composition different from the dopant *e.g.* Li₂NiF₄ in LiF:NiF₂ (Jehanno and Perio 1969) and M₂CoCl₄ or M₃CoCl₅ in cobalt doped alkali halide crystals (Musa 1965, 1966; Trutia and Voda 1976).

The precipitates in cobalt doped alkali halides have been identified through optical absorption studies. However, recently we (Gupta and Pandey 1980) have shown that all the added cobalt gets precipitated in RbCl crystals containing even a low dose (60 ppm) of such impurity ions.

The purpose of the present work is to report the results of electrical conductivity measurements in heavily doped RbCl:CoCl₂ crystals. This system is quite interesting because in this case the radius of the impurity ion is much less than that of the host cation (Co²⁺ — 0.72 Å and Rb⁺ — 1.48 Å) and as explained in our earlier paper (Gupta and Pandey 1979) the doped ion could initially occupy an interstitial site in the lattice which may finally lead to the creation of precipitates of the composition Rb₂CoCl₄ or other types.

2. Experimental

The RbCl:CoCl₂ crystals with two concentrations of cobalt were grown in vacuum by Stockbarger technique using G. R. grade RbCl (E. Merck, Germany) as the host material. The platelets of size 1 × 1 × 0.2 cm³ were cut from the parent chunk of the crystal and found to be translucent containing blue coloured islands of different sizes, clearly seen under a microscope. The cobalt impurity concentration was determined through atomic absorption spectroscopy at Regional Sophisticated Instrumentation Centre, Madras, India and the crystals were found to contain an average concentration of 2500 ppm and 6000 ppm. The crystal with 2500 and 6000 ppm of cobalt are here referred as R2500 and R6000 respectively.

For conductivity measurements the opposite faces of the crystals were coated with silver paint with a camel-hair fine artist's brush taking care that the paint did not spread over the sides. To avoid any possibility of leakage through silver paint sticking to walls, the edges of the crystals were cleaved off. Further, the crystals were placed between thin platinum foil strips. The d.c. electrical conductivity measurements were made using an ECIL EA 815 Electrometer Amplifier. The current through the crystal was measured as a function of temperature only when it attained thermal equilibrium which was achieved with the help of an APLAB 9601 temperature controller. The exact temperature of the sample was determined using a portable Toshniwal PL 52 potentiometer by measuring the thermo e.m.f. of a Chromel/Alumel thermocouple kept very close to it. The maximum error in the measurement of temperature was 0.25°C upto 450°C and 2.5°C for higher temperatures. The polarization effects inherent in the d.c. measurements were avoided by applying the electric field across the crystal only for a short duration of time (less than 30 sec) and keeping it short circuited between the consecutive observations.

3. Results and discussion

Through conductivity measurements we have earlier shown (Gupta and Pandey 1980) that cobalt has a strong tendency to precipitate and it was found that all the 60 ppm of cobalt added in RbCl host forms precipitates. These precipitates have been thought to be of composition Rb₂CoCl₄ or Rb₃CoCl₅ as reported by Musa (1965, 1966) and Trutia and Voda (1976). We have also suggested a model (Gupta and

Pandey 1979) which helps to understand the creation of Rb_2CoCl_4 precipitates during the crystal growth itself.

Figure 1 shows the conductivity plots of $\log \sigma T$ vs $1000/T$ for three crystals *viz.* pure RbCl, RbCl:CoCl₂ with 2500 ppm of cobalt (R2500) and RbCl:CoCl₂ with 6000 ppm of cobalt (R6000). As shown in this figure the conductivity plot for pure RbCl contains two regions represented by intrinsic region I and extrinsic unassociated region II, their slopes being given as $E_c + W_s/2$ and E_c respectively. The slope of the region II gives the value of the energy of migration of a cation vacancy which has been found to be 0.82 eV. Further, the slope of the region I is 1.90 eV. From the slopes of these two regions the energy of formation of Schottky defects, W_s , has been calculated to be 2.16 eV.

The conductivity plots for R2500 and R6000 crystals match exactly from the beginning of the temperature of measurement upto 360°C indicating that in this temperature range the number of charge carriers is about the same in the two crystals. Beyond 360°C, however, the plot of a R6000 crystal separates out from that of R2500 showing an increase in conductivity. Therefore, the extra concentration to the tune of 3500 ppm of cobalt in a R6000 crystal does not contribute at all to the number of charge carriers upto 360°C, but does so only above this temperature. Accordingly, it seems that in a R6000 crystal about 3500 ppm of cobalt remains in a precipitate form upto 360°C. The idea of precipitate formation is further supported by the photomicrographs taken in these crystals (figures 2 and 3a, b). The precipitates are seen in both

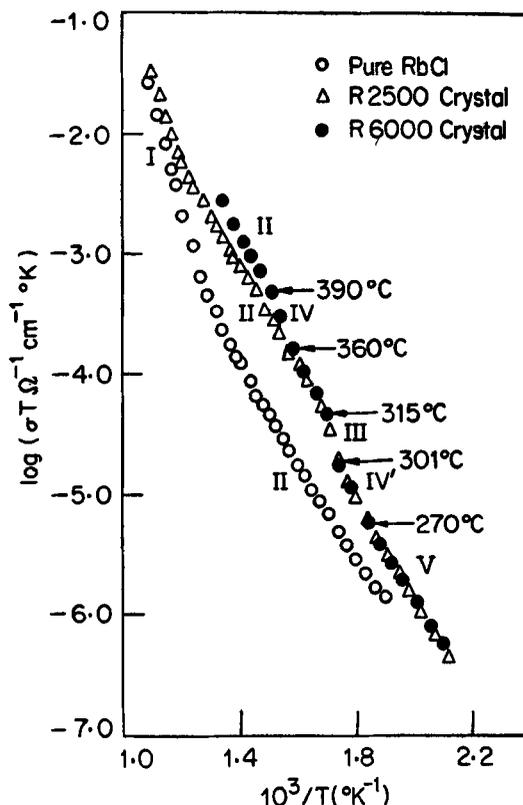


Figure 1. Conductivity plots for pure RbCl crystal, RbCl crystal doped with 2500 ppm of cobalt (R2500) and RbCl crystal doped with 6000 ppm of cobalt (R6000).

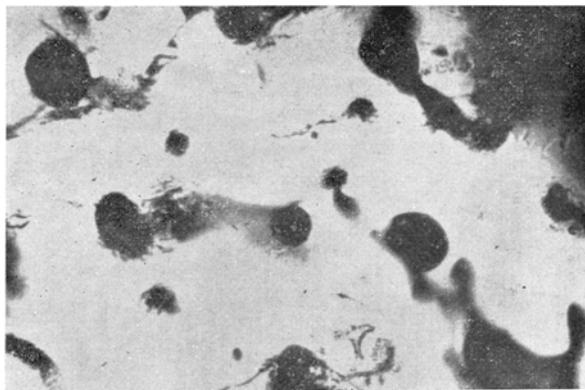
R6000 and R2500 crystals; but as it is clear from figures 2 and 3a, b the precipitates in a R6000 crystal are quite large in size as compared to those in a R2500 crystal. It appears that a R6000 crystal contains extra precipitates of a variety different from those in a R2500 crystal.

In contrast to a R2500 crystal a relatively sharp increase in conductivity is observed in a R6000 crystal in the temperature range 360–390°C, the slope of this region being 1.20 eV. This appears to be due to the dissolution of a particular type of precipitate in these crystals and may thus be termed as region IV. Beyond 390°C, a region with slope 0.80 eV has been observed upto 470°C and termed as region II for this crystal. The slope of this region is equal to that of region II for a pure RbCl crystal.

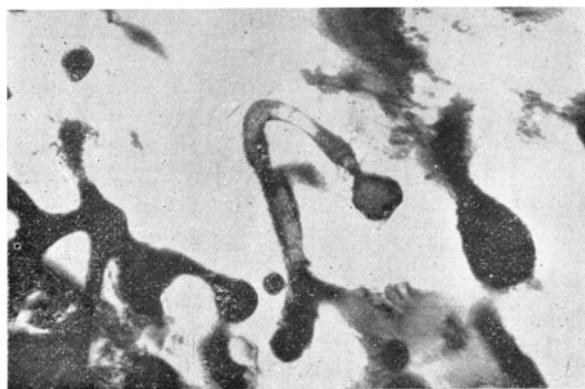
In the case of R2500 crystal a region with slope 0.80 eV is obtained in the temperature range 315°C to 490°C. This region has been termed as region II of R2500 crystal, its slope being also equal to that of the corresponding region in a pure RbCl crystal. At the lowest temperatures from 203°C upwards a region with the slope 0.83 eV is obtained and has been ascribed as region V, since the slope of this region is also very close to that of region II for a pure RbCl crystal (Dreyfus and Nowick 1962). From 315°C downwards *i.e.* below region II, a prominent region exists and has been designated as region III *i.e.* the extrinsic associated region. There should, further, be a region IV in the conductivity plot between the regions III and V. It appears that in our samples this region IV' (so called because there is already one as IV) has a very narrow temperature range from 270°C to 301°C. This region IV' is common to both R6000 and R2500 crystals and corresponds to a different type of precipitate from the one which has earlier been explained to occur exclusively in R6000 crystals beyond 360°C. Finally for completeness the region between 315°C and 360°C of R6000 crystal which coincides with that for R2500 crystal should be termed as another V instead of II.

The slope of the region III, as described above, has been found to be 1.20 eV. From the slopes of region II (E_c) and III($E_c + W_a/2$) the association energy of the Co^{2+} impurity and cation vacancies turns out to be 0.80 eV. To the best of our knowledge, such a high value of W_a has not been reported in alkali halide hosts doped with divalent metal ions which normally substitute for alkali ions. However, the experimental values of W_a as 0.70 eV and 0.72 eV for RbCl doped with Pr^{3+} (Radhakrishna and Sharma 1974) and Bi^{3+} (Radhakrishna and Srinivasa Setty 1976) respectively are close to our value. In both these cases two cation vacancies are produced for each trivalent cation in order to meet the charge neutrality condition. A high value of 0.80 eV for W_a is expected in the case where a Co^{2+} is associated with two cation vacancies. Such a situation can be realised if Co^{2+} occupies an interstitial site in RbCl host. As described earlier (Gupta and Pandey 1979) the existence of precipitates of Rb_2CoCl_4 is also related to the interstitial occupancy of Co^{2+} in RbCl.

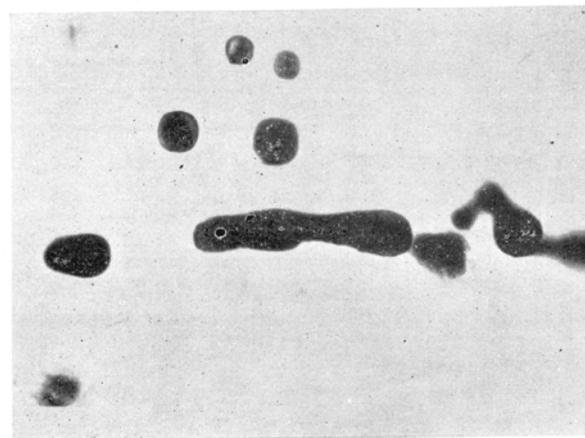
Table 1 lists the values of energy parameters W_s , E_c and W_a for pure RbCl and RbCl crystals doped with different impurities (Radhakrishna and Srinivasa Setty 1976; Fuller 1970; Mishra and Sharma 1974; Shukla and Rao 1974) as obtained through conductivity measurements. It is evident from this table that the values of W_s obtained by us in RbCl are in excellent agreement with those reported by other workers, the only exception being the value obtained by Radhakrishna and Srinivasa Setty (1976) in Bi^{2+} doped RbCl. The energy of migration E_c of a cation vacancy as determined by various authors varies from 0.54 eV to 0.99 eV. Such an observed variation in E_c is quite large, and calls for a systematic and thorough re-examination



(2)



(3a)



(3b)

Figure 2. Photomicrograph ($\times 100$) of a RbCl crystal doped with 2500 ppm of cobalt (R2500).

Figures 3a, b. Photomicrograph ($\times 40$) of a RbCl crystal doped with 6000 ppm of cobalt (R6000).

Table 1. Energy parameters (W_s , E_c and W_a) obtained from conductivity measurements in pure and doped RbCl crystals.

Crystal system	W_s (eV)	E_c (eV)	W_a (eV)	Reference
RbCl:Bi ²⁺	1.85	0.85	0.58	Radhakrishna and Srinivasa Setty 1976
RbCl:Sr ²⁺	2.04	0.54	0.64	Fuller 1970
RbCl:Pb ²⁺	2.12	0.99	0.49	Mishra and Sharma 1974
Pure RbCl	2.12	0.93	...	Shukla and Rao 1974
	2.16	0.82	...	Present work
RbCl:Co ²⁺	...	0.80	0.80	Present work

of this problem. Furthermore, the activation energy E for the jump of cation vacancy bound to the impurity ion in RbCl: Co²⁺ system as determined by us (Gupta and Pandey 1979) through dielectric loss measurements is as low as 0.63 eV. This now seems to be only an effective value and the observed loss pattern can be explained to be due to the combined effect of different individual loss peaks, one of these corresponding to the jump of vacancy bound to the Co²⁺ ion with E as 0.80 eV, the value from conductivity measurements and the other due to the impurity-vacancy exchange with a lower value (Gupta 1980) of 0.51 eV. The value of W_a lies in the range 0.49 eV to 0.80 eV. The high value of 0.80 eV for W_a in this system has been discussed earlier and is probably due to interstitial occupancy of Co²⁺ in RbCl.

Both the type of crystals R2500 and R6000 appeared blackened at the surface after thermal treatment during the measurements and this blackness has been found to be due to the expulsion of cobalt from the bulk of the crystal to its surface. The blackness was, however, more in a R6000 crystal as compared to that in a crystal of R2500 variety.

Yacaman *et al* (1976) have reported that divalent metal ions *e.g.* Mn²⁺, Fe²⁺ etc imbedded in an alkali halide crystal tend to migrate to the surface of the crystal when it is heated between 300–700°C in the atmosphere of air or nitrogen or even in vacuum. During such a heating process, the divalent metal ions have a tendency to move within the lattice and the ions which happen to come close to the crystal surface emerge out from it and get oxidized. Thus a concentration-gradient of impurities is produced in the crystal, resulting in an outflux of ions towards the surface and finally in the formation of an oxide film on the surface. Such oxide films have been studied in detail by Yacaman *et al* (1976) using several techniques *viz.* scanning (SEM) and transmission (TEM) electron microscopy and high energy electron diffraction (HEED). It is seen that such a phenomenon of diffusion of impurities to the surface (expulsion) does not occur in the crystal during its growth. It is further observed that expulsion occurs only in cleaved samples.

Ocanaz *et al* (1976) have reported the formation of two kinds of oxide films on heat treatment of NaCl:Co²⁺ crystals. When heating is done at 450°C for 15 min to 14 hr a Co₃O₄ film is produced on the NaCl surface; while heating at a higher temperature (650°C) for about 6 hr results in the formation of a film of a different kind of oxide, CaO, as well. Further, the two types of oxides have been found to coexist at the NaCl surface. The oxides form crystallites and their size increases with temperature and heating period. No major difference has been observed whether the crystals are heated in air or in nitrogen atmosphere.

We have observed expulsion of cobalt in all the crystals of $\text{RbCl}:\text{CoCl}_2$ studied. The expulsion has also been studied through scanning electron microscopy. The micrograph showed a random and heterogeneous distribution of crystallites over the total field of view of the microscope. But it has not been possible to determine the exact composition of the crystallites. As our crystals are heated only upto 450°C we expect the crystallites to be of Co_3O_4 by analogy with the results of Ocana *et al* (1976).

It will be of worth to mention that the conductivity measurements in R6000 crystal could not be continued beyond 470°C because for such temperatures the current through the crystal increased abnormally. This abnormal increase in current seems to be due to the combined effect of the coating of silver paint over the crystal surface and the expulsion of cobalt from them. Such abnormality was not found in R2500 crystals. Further work on these lines is in progress and will be reported elsewhere.

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References

- Al-Jammal Y 1976 D. Phil Thesis, Sussex University
 Chapman J A and Lilley E 1975 *J. Mater. Sci.* **10** 1154
 Dreyfus R W and Nowick A S 1962 *Phys. Rev.* **126** 1367
 Fuller R G 1970 *Bull. Am. Phys. Soc.* **15** 384
 Gupta S K and Pandey S D 1979 *J. Phys. (Paris)* **40** 779
 Gupta S K and Pandey S D 1980 *J. Phys. Chem. Solids* **41** 811
 Gupta S K 1980 *Conductivity and dielectric loss studies in doped crystals* Ph.D. Thesis, Kanpur University
 Hartmanova M 1971 *Phys. Status Solidi* **A7** 303
 Hensel G and Ziller J 1968 *Phys. Status Solidi* **30** K165
 Jain S C, Lal K and Mitra V 1970 *J. Phys. Chem.* **3** 2420
 Jehanno G and Perio P 1969 *Bull. Soc. Fr. Mineral Cristallogr.* **91** 5
 Laredo E and Dartyge E 1971 *Acta Crystallogr.* **A27** 353
 Lilley E and Newkirk J B 1967 *J. Mater. Sci.* **2** 567
 Mishra K D and Sharma M N 1974 *J. Phys. Soc. Jpn.* **36** 154
 Musa M 1965 *Phys. Status Solidi* **9** K175
 Musa M 1966 *Phys. Status Solidi* **A16** 771
 Ocana T, Guillen M and Yacaman M J 1976 *J. Cryst. Growth* **34** 103
 Radhakrishna S and Sharma B D 1974 *Phys. Rev.* **139** 2073
 Radhakrishna Sand Srinivasa Setty 1976 *Phys. Rev.* **814** 969
 Shukla A K and Rao C N R 1974 *J. Chem. Soc. Faraday Trans. 2* **70** 1628
 Sors A I 1973 Ph.D. Thesis, Sussex University
 Suzuki K 1961 *J. Phys. Soc. Jpn.* **16** 67
 Swamy Rao K N and Parasnis A S 1969 *J. Electrochem. Soc.* **116** 503
 Swamy Rao K N and Parasnis A S 1978 *Philos. Mag.* **37** 769
 Trutia A and Voda M 1976 *J. Chem. Phys.* **64** 2715
 Yacaman M J, Gomez A and Bassett G A 1976 *Thin Solid Films* **35** 37