PROC. JSSF-2, KYOTO, 1980
J. PHYS. SOC. JPN. **49** (1980) SUPPL. B, pp. 102–105.

Phase Transitions in Langbeinite-Type Compounds

Noboru YAMADA, Tomoyuki HIKITA, Masaki MAEDA and Takuro IKEDA

Department of Applied Physics, Faculty of Engineering
Tohoku University, Sendai 980

The phase transitions in five langbeinite-type crystals, $(NH_4)_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$, $K_2Co_2(SO_4)_3$, and $K_2Ca_2(SO_4)_3$ have been examined by optical, pyroelectric and dielectric measurements. The symmetry of the lowest temperature phase in $Rb_2Cd_2(SO_4)_3$ and $K_2Zn_2(SO_4)_3$ is assigned as orthorhombic $P2_12_12_1$. Ferroelectricity and a phase transition are found in $K_2Co_2(SO_4)_3$ and $K_2Ca_2(SO_4)_3$, respectively. Crystals of the langbeinite family are classified into three groups according to the transition scheme. It is found that the transition temperature to the orthorhombic phase is linearly related to $r_A - r_B$ and the appearance of ferroelectricity is restricted to the range of $r_A - r_B$ between 0.45 Å and 0.51 Å, where r_A and r_B are the ionic radii of monovalent and divalent cations, respectively.

§1. Introduction

A large number of double sulphate crystals with the general formula $A_2^{1+}B_2^{2+}(SO_4)_3$ are isomorphous with the mineral langbeinite and form the langbeinite family.[1] Up to the present, nine compounds have been reported to undergo phase transitions.[2] However, information on the transition behavior is not enough for us to understand the transition mechanism of this family.

The purpose of the present paper is to examine the key feature of the transition scheme of this family and also to make a morphological classification of those transition in connection with the ionic radii of constituent ions.

§2. Experiments

Transition schemes were investigated on five compounds $(NH_4)_2Cd_2(SO_4)_3$, $Rb_2Cd_2(SO_4)_3$, $K_2Zn_2(SO_4)_3$, $K_2Co_2(SO_4)_3$ and $K_2Ca_2(SO_4)_3$ (abbreviated here as ACS, RCS, KZS, KCoS and KCaS, respectively). Single crystals of ACS and RCS were grown at 85°C by the evaporation method. Those of KZS and KCoS were obtained by the Czochralski and Bridgman methods, respectively.

Dielectric measurement was made at 1 kHz using a low capacitance bridge. Spontaneous polarization was measured by the pyroelectric charge method. Measurements of the optical birefringences wee made with Babinet compensator.

§3. Results

A new phase transition has been recently reported in RCS at −205°C.[3] In order to examine the symmetry of the phase below the temperature, the measurement of spontaneous polarization[4] and optical observation were extended to lower temperatures and the result of the former is shown in Fig. 1. As seen from Fig. 1, the lowest temperature phase is nonpolar. In this phase, we could observe the three types of domains A, B and C, of which the extinction positions are parallel to one of the cubic axes. Therefore, the symmetry of the lowest temperature phase is assigned as orthorhombic $P2_12_12_1$. Therefore, it is concluded that RCS transforms successively in the order of I, II, III and IV, where I, II, III and IV represent cubic $P2_13$,

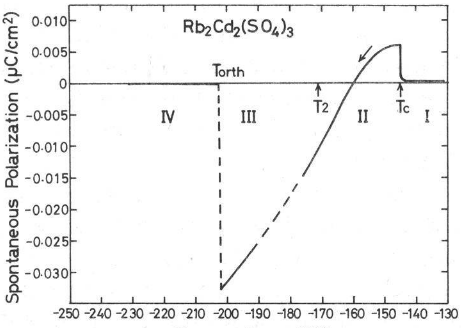

Fig. 1. Temperature dependence of spontaneous polarization of $Rb_2Cd_2(SO_4)_3$.

monoclinic $P2_1$, triclinic $P1$ and orthorhombic $P2_12_12_1$ phases, respectively. The spontaneous polarization P_s in III phase was obtained in the present experiment. Around the transition temperature from II to III, the domain structures were complex and the P_s was not clearly determined, as seen by dotted curve in the figure.

The measurement of spontaneous polarization P_s and the optical observation of KZS were made over the temperature range from 20°C to −260°C. The result of the measurement of P_s is shown in Fig. 2. The lowest temperature phase below −188°C is nonpolar. The domains in this phase are quite similar to those in the IV phase of RCS. Thus, the lowest temperature phase in KZS is assigned also as the orthorhombic IV. Taking account of the change of the extinction position associated with the reversal of polarization, the phase between T_c and −188°C is believed to be the phase II.[5] Any phase corresponding to the phase III has not been found by the present careful investigations including elastic measurements. Thus, it is concluded that KZS transforms successively in the order of I→II→IV.

It is known that KCoS undergoes the phase transition at −148°C[6] and the transition is of a type from cubic to nonpolar phase.[2] The result of pyroelectric measurement is shown in Fig. 3. It is obvious that the low temperature phase is polar. The sign of the polarization was reversed by the electric field. Therefore, this transition is a ferroelectric one. Further, a large dielectric anomaly indicative of phase transition from ferroelectric phase to IV phase was found at the vicinity of liquid helium temperature. Thus, the transition of KCoS seems to be the I→II(→III)→IV type.

The phase transition of KCaS was examined by the measurement of birefringence. The birefringence of KCaS vanishes above 200°C. It is known that the symmetry of this compound is orthorhombic $P2_12_12_1$ at room temperature. Therefore, the phase transition at 200°C is assigned as that from orthorhombic IV to cubic I.

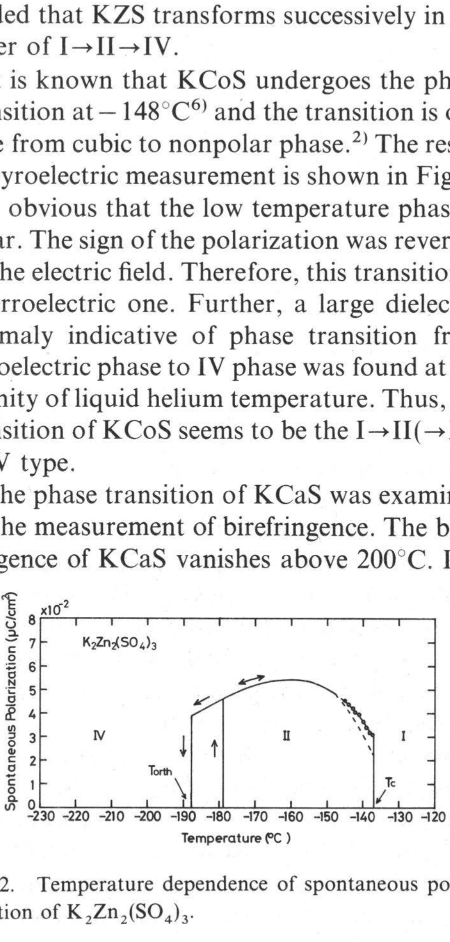

Fig. 2. Temperature dependence of spontaneous polarization of $K_2Zn_2(SO_4)_3$.

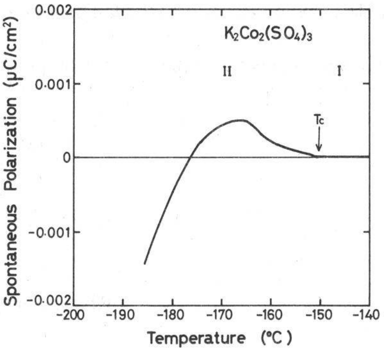

Fig. 3. Temperature dependence of spontaneous polarization of $K_2Co_2(SO_4)_3$.

As for the ACS, measurements of spontaneous polarization P_s and dielectric constant ε were extended to temperatures below liquid nitrogen temperature. No changes of P_s and ε indicative of phase transitions were found down to liquid helium temperature. The transformation of ACS is confirmed to be only from the cubic to monoclinic phase, in agreement with the result of lattice strain measurements by Kobayashi *et al.*[7]

§4. Discussion and Conclusion

The transition schemes in the crystals of langbeinite family are now determined. They are classified into three groups as shown in Table I.

The crystals of the group 1 transform directly from the cubic phase I to nonpolar orthorhombic phase IV. The transitions of crystals in the group 2 are characterized by the successive transformations from paraelectric cubic phase I to ferroelectric phases and finally to nonpolar IV phase. Here, we assign the ACS to be in the group 2, though the orthorhombic phase IV could not be found. The crystals exhibiting no transition are grouped together as the group 3.

Here, we notice that the lowest temperature phase is always orthorhombic with only one exception of ACS and the ferroelectric phases appear in the intermediate temperature range between those for the cubic and orthorhombic phases. The transition from the cubic to or-

Table I. Classification of the langbeinite family according to transition scheme.

Group	Transition Scheme	Compound	Abbrev.	Transitions
1	I→IV	$K_2Mn_2(SO_4)_3$	KMS	−72°C: IV | I
		$K_2Cd_2(SO_4)_3$	KCS	159°C: IV | I
		$Rb_2Ca_2(SO_4)_3$	RCaS	−90°C: IV | I
		$K_2Ca_2(SO_4)_3$	KCaS	187°C*: IV | I*
2	I→II	$(NH_4)_2Cd_2(SO_4)_3$	ACS	−178°C: * II | I
	I→II→III→IV	$Tl_2Cd_2(SO_4)_3$	TCS	−181°C, −153°C, −145°C: IV | III | II | I
		$Rb_2Cd_2(SO_4)_3$	RCS	−205°C, −170°C, −144°C: IV* | III | II | I
	I→II(→III)→IV	$K_2Zn_2(SO_4)_3$	KZS	−188°C, −135°C: IV* | II* | I
		$K_2Co_2(SO_4)_3$	KCoS	−148°C: IV* | II* | I
3	None	$K_2Mg_2(SO_4)_3$ $Cs_2Ca_2(SO_4)_3$ $(NH_4)_2Mg_2(SO_4)_3$ $Tl_2Mn_2(SO_4)_3$ ⋮	KMgS CsCaS AMgS TMS	

I: $P2_13$, II: $P2_1$, III: $P1$, IV: $P2_12_12_1$
* present study

thorhombic phase IV seems to be rather more fundamental feature of the langbeinite family than the ferroelectric transition.

Recently we have made the structure analysis of $K_2Mn_2(SO_4)_3$ both in cubic and in orthorhombic phases.[8] The analysis revealed that the average manganese-oxygen distance is greater in the orthorhombic IV phase than in the cubic I phase. However, in the case of the average potasium-oxygen distance, the situation is reversed. This seems to suggest that the stability of the phases in langbeinite-type crystals depends on the difference of the ionic radii between the constituent cations.

The transition temperatures are plotted as a function of the difference in ionic radii of the constituent ions, as shown in Fig. 4, where r_A and r_B are ionic radii of A and B ions. Open circles show the transition temperatures T_{orth} from cubic I to orthorhombic IV phase in the group 1 crystals and closed circles correspond to the transition temperatures to the orthorhombic IV phase in the group 2 crystals. The open circles obviously lie on a straight line and the closed circles are scattered in the vicinity of the extrapolated line from this T_{orth} line. Open triangles represent the Curie temperature T_c and they are confined a narrow temperature range. Though T_c is almost independent of $r_A - r_B$, it is interesting to note that the appearance

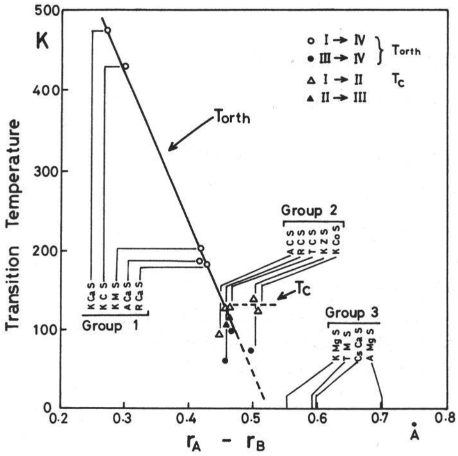

Fig. 4. Transition temperature versus r_A—r_B.

of ferroelectric phase is restricted to the range of ionic radius difference between 0.45 Å and 0.51 Å. In the crystals for the difference larger than 0.51 Å, no transitions are found.

In conclusion, the results of the present study are summarized. The lowest temperature phases in $Rb_2Cd_2(SO_4)_3$ and $K_2Zn_2(SO_4)_3$ are assigned as orthorhombic $P2_12_12_1$. The I→IV phase transition and the ferroelectricity were found in $K_2Ca_2(SO_4)_3$ and $K_2Co_2(SO_4)_3$, respectively. Crystals of the langbeinite family are classified into the three groups according to the transition scheme in connection with $r_A - r_B$. The transition temperature to orthorhombic IV phase has a linear relation with $r_A - r_B$. The appearance of ferroelectricity is restricted in the range of $r_A - r_t$ between 0.45 Å and 0.51 Å and the Curie temperature is confined to the narrow temperature range around − 145°C.

References

1) H. F. McMurdie, M. C. Morris, J. de Groot and H. E. Swanson: J. Res. Natl. Bur. Stand. **A75** (1971) 435.
2) T. Hikita, H. Sekiguchi and T. Ikeda: J. Phys. Soc. Jpn. **43** (1977) 1327.
3) M. Maeda: J. Phys. Soc. Jpn. **49** (1980) 1090.
4) N. Yamada: J. Phys. Soc. Jpn. **46** (1979) 561.
5) M. Glogarova and J. Fousek: Phys. Status Solidi (a) **15** (1973) 579.
6) B. Březima, A. Fouskova: Kristall und Technik **13** (1978) 623.
7) J. Kobayashi, Y. Uesu, H. Miyazaki and T. Hosokawa: Ferroelectrics **21** (1978) 515.
8) N. Yamada, M. Maeda and H. Adachi: To be submitted to J. Phys. Soc. Jpn.