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Phase Transitions in a $Cs_{2-x}K_{1+x}BiCl_6$ Solid Solution

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A solid solution with a $Cs_{2-x}K_{1+x}BiCl_6$ ($0 \leq x \leq 1$) formulation and an elpasolite-related structure was prepared. At room temperature the symmetry is cubic ($Fm3m$) for $x = 0$ and triclinic ($P\bar{1}$) for $x \neq 0$. For $0 \leq x \leq 1$, various techniques enabled us to detect a phase transition of the ferroelastic–paraelastic type at t_c (°C) temperature. The t_c and ΔH_{t_c} values are correlated to the size of the alkali ions.

Introduction

Chlorides with an A_2BMCl_6 formulation, A and B being alkali elements and M a transition or a rare earth element, have been the topic of several crystallographic and physical studies (*1–17*). For most compounds, $r_{A+} > r_{B+}$ and the materials have an elpasolite-type structure at room temperature. The corresponding symmetry is generally cubic but in some cases a symmetry lowering (to tetragonal or hexagonal) can be observed (*6, 8–10, 12–17*). Furthermore, some recent investigations on nonlinear properties of materials with formula $(A,B)_3MX_6$ (A,B = alkali or alkali earth element; X = O, F, Cl, Br) show the existence of:

—ferroelastic properties for the A_2BMF_6-type fluorides (A,B = alkali metal) (*18*);

—ferroelastic and ferroelectric properties for the oxide fluorides $A_2BMO_3F_3$ (A,B = alkali metal, M = Mo,W) (*19*);

—piezoelectric and nonlinear optical properties for the oxide $Sr_{3-x}Ba_xWO_6$ (*20*); and

—ferroelastic properties for the chlorides A_2BMCl_6 (*6, 10, 12–17*) or the bromides A_2BMBr_6 (*21*).

The transition temperatures where the nonlinear properties appear are sometimes above room temperature, which is worthwhile from the point of view of applications (*22*).

Only a few A_2BBiCl_6 bismuth chloride compounds were synthesized (*3, 9*). The single crystal structure determination of $Cs_2NaBiCl_6$ (*5*) confirmed the cubic $Fm3m$ symmetry at room temperature, and a ferroelastic phase transition was observed on the same compound at low temperature (*10, 16*). Therefore we studied the phase transitions in chlorides of $(A,B)_3MCl_6$ formulation, M being bismuth; its compounds

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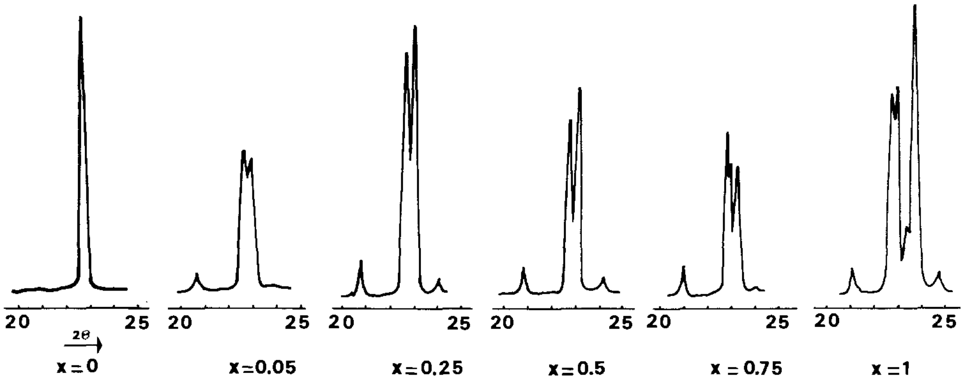

FIG. 1. Splitting of the (220) reflection (*f.c.c.* phase) versus composition.

are generally stable to air moisture at room temperature and have a low melting point, which makes sintering and crystallization easier. Furthermore, the anisotropic electronic configuration of the Bi^{3+} ion, which has a lone pair, gives rise to local electrical dissymmetry in the crystal lattice.

We first chose to study the Cs_2KBiCl_6–CsK_2BiCl_6 system. Cs_2KBiCl_6 is isostructural with $Cs_2NaBiCl_6$ (*5*):cubic (*Fm*3*m*) elpasolite-type structure, with the Bi^{3+} and K^+ ions in sites of perfect octahedral symmetry (4*a* and 4*b* sites, respectively), while the Cs^+ ions occupy all the 12-coordinate sites (8*c* sites).

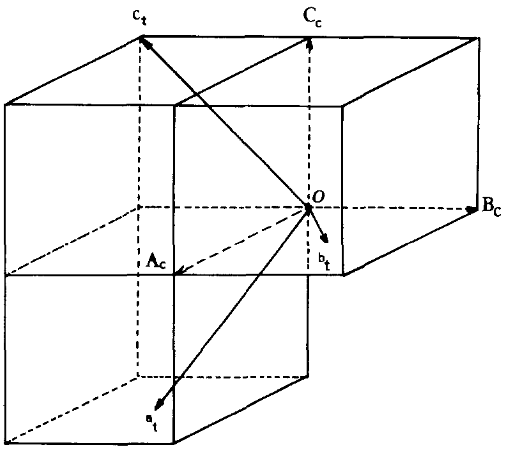

FIG. 2. Cubic and triclinic unit cells of the $Cs_{2-x}K_{1+x}BiCl_6$ phases ($a_{\text{tricl.}} = 0a_t$; $b_{\text{tricl.}} = 0b_t$; $c_{\text{tricl.}} = 0c_t$; $a_{\text{cub.}} = 0A_c = 0B_c = 0C_c$).

Experimental

The starting materials (anhydrous chlorides $BiCl_3$, CsCl, KCl > 99.9%) were manipulated in a dry box. Reactions were performed in sealed quartz tubes either at 700°C (in molten state) for 2 hr, or at 580°C (in solid state). In the latter case, the obtained products were ground and reheated several times. The materials were stable to air moisture at room temperature. The purity of the samples was checked by X-ray powder diffraction method using a Philips diffractometer with monochromatized Cu*Kα* radiation. The samples were scanned at a rate of 0.5° (2*θ*) min^{-1}.

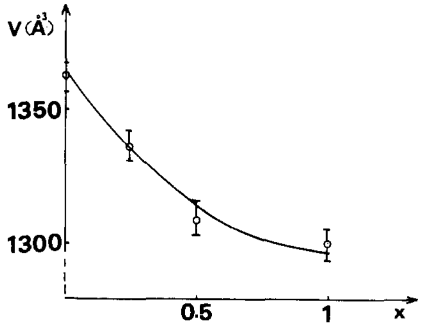

FIG. 3. Unit cell volume variation vs *x*.

TABLE I

CRYSTALLINE SYSTEMS AND CELL PARAMETERS AT 20°C

Phase	System	Cell parameters (Å and degrees) and V (Å^3) with esd	Z
Cs_2KBiCl_6	Cubic	a = 11.086 (5) V = 1353 (10)	4
$Cs_{1.75}K_{1.25}BiCl_6$	Triclinic	a = 13.62 (13), α = 119.5 (6) b = 7.72 (2), β = 106.9 (6) c = 15.46 (3), γ = 90.0 (5) V = 1334 (25)	4
$Cs_{1.5}K_{1.5}BiCl_6$	Triclinic	a = 13.556 (12), α = 119.70 (6) b = 7.664 (9), β = 106.26 (6) c = 15.320 (13), γ = 90.34 (6) V = 1307 (10)	4
CsK_2BiCl_6	Triclinic	a = 13.503 (10), α = 119.15 (5) b = 7.643 (8), β = 106.36 (5) c = 15.278 (11), γ = 90.54 (5) V = 1301 (10)	4

The study of phase transitions was carried out by various techniques:

—X-ray diffraction studies versus temperature (powder samples) with a Guinier camera;

—birefringence using polarized light with a Leitz Ortholux II Pol optical microscope; and

—thermal analysis with a Perkin–Elmer differential scanning calorimeter (DSC 2). The temperature calibration was performed with In (mp: 151°C), Sn (232°C), and Na_2CrO_4 (tr.p.: 671°C). Enthalpy calibration was achieved from the known latent melting heat of In (28.4 J g^{-1}). The heating and cooling rates used were 20° min^{-1} with sample amounts between 20 and 40 mg. Studies between liquid nitrogen temperature and 500°C were performed with Al pans, and with Au pans for higher temperatures.

DTA of samples sealed in vacuum in quartz tubes was taken with a Linseis L 61/10 apparatus.

Dielectric measurements under dry argon were taken with a Wayne–Kerr B 64 bridge working at 1600 Hz. The samples were 6 mm in diameter and 1.5-mm thick pellets, obtained by 2 hr sintering at 550°C under argon. Their compactness exceeded 0.9.

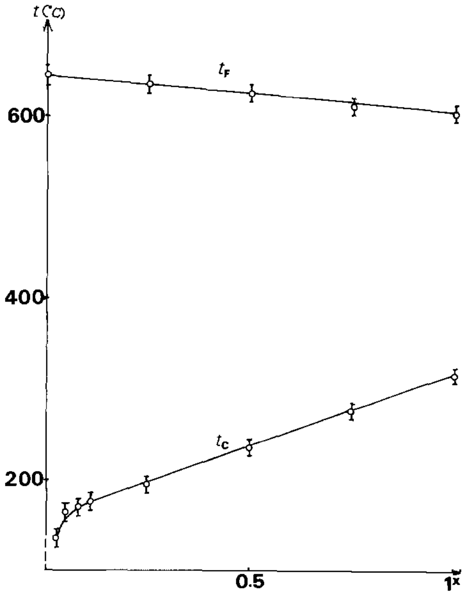

FIG. 4. Phase transition temperature t_c and melting point t_F variations vs x.

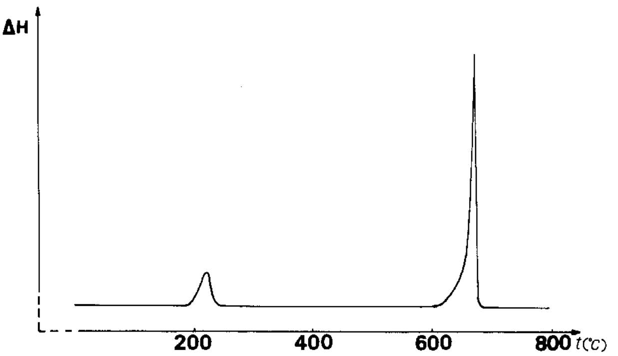

FIG. 5. DTA thermogram of $Cs_{1.75}K_{1.25}BiCl_6$ (ΔH scale in arbitrary units).

Results and Discussion

A continuous solid solution with formulation $Cs_{2-x}K_{1+x}BiCl_6$ ($0 \leq x \leq 1$) and an elpasolite-related structure were detected by X-ray powder diffraction. While Cs_2KBiCl_6 ($x = 0$) is cubic at room temperature, the X-ray diffraction pattern is much more complex for $0 < x \leq 1$. Figure 1 shows the splitting of the (220) reflection (in *f.c.c.* phase) versus composition. The existence of four components as soon as $x = 0.05$ implies at least a monoclinic distortion, while the existence of more components when x increases (five for $x = 0.75$ and six for $x = 1$) suggests a triclinic deformation. As it was unreasonable to index and determine the lattice parameters of a triclinic cell from an X-ray powder diffraction pattern, we tried to prepare single crystals by slow cooling (5°/hr) of melts in vacuum-sealed quartz tubes. The crystals obtained were systematically checked by Laüe, rotation, and Weissenberg methods. Despite the classical troubles inherent to ferroelastically twinned crystals, we managed to select "single-domain" crystals of good quality for compositions $x = 0.25$, 0.5, and 1. The triclinic symmetry was confirmed for each phase. Accurate unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections measured on a Philips PW 1100 four-circle automatic diffractometer. Crystal data are listed in Table I.

Work is in progress to try and solve the crystal structure of CsK_2BiCl_6. Figure 2 gives the relationship between triclinic and cubic cells. The vector relations and the transformation matrices are

$$\mathbf{a}_t = \frac{\mathbf{A}_c}{2} - \frac{\mathbf{B}_c}{2} - \mathbf{C}_c,$$

$$\mathbf{b}_t = \frac{\mathbf{A}_c}{2} + \frac{\mathbf{B}_c}{2},$$

$$\mathbf{c}_t = -\mathbf{B}_c + \mathbf{C}_c,$$

and

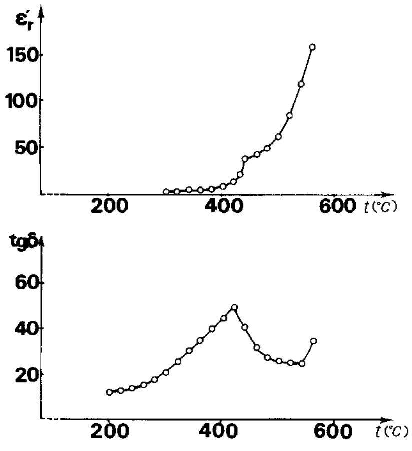

FIG. 6. Dielectric constant (ϵ'_r) and dielectric losses ($tg\delta$) vs temperature of a CsK_2BiCl_6 ceramic (at 1600 Hz).

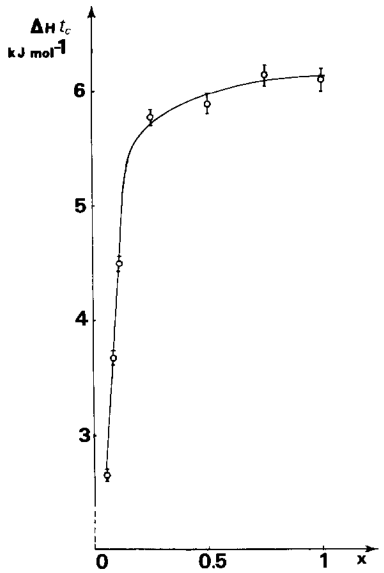

FIG. 7. Variation of the enthalpy transition vs x.

$$\begin{pmatrix} a_t \\ b_t \\ c_t \end{pmatrix} = \begin{pmatrix} 1/2 & -1/2 & -1 \\ 1/2 & 1/2 & 0 \\ 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} A_c \\ B_c \\ C_c \end{pmatrix},$$

from which it is possible to deduce the inverse matrix

$$\begin{pmatrix} A_c \\ B_c \\ C_c \end{pmatrix} = \begin{pmatrix} 1/2 & 3/2 & 1/2 \\ -1/2 & 1/2 & -1/2 \\ -1/2 & 1/2 & 1/2 \end{pmatrix} \begin{pmatrix} a_t \\ b_t \\ c_t \end{pmatrix}.$$

The space group was determined by a nonlinear optical test using powders[1] according to the method described by Kurtz and Perry (*23*). All solid solutions showed no second harmonic generation, which means that they are probably centrosymmetrical. One may conclude that the space groups are $Fm3m$ for $x = 0$ and $P\bar{1}$ for $0 < x \leq 1$. Figure 3 shows that the volume of the unit cell (Table I) decreases with x, which can be explained by the decreasing size from Cs^+ to K^+.

One reversible phase transition at temperature t_c (°C) was detected for $x > 0$ by the earlier-described techniques. For $x = 0$ no phase transition was detected between liquid nitrogen and room temperature either by X-ray diffraction or DSC measurements. Variation with composition of the transition temperatures t_c and of the melting points t_F determined by DSC are given in Fig. 4. Figure 5 shows the DTA diagram for $x = 0.25$. Figure 6 shows the dielectric constant (ϵ'_r) and dielectric loss ($tg\delta$) variations for $x = 1$; slight anomalies in dielectric measurements are found near t_c.

Above t_c, the crystallographic distortion disappears and we may assign the X-ray diffraction pattern to a cubic (*f.c.c.*) symmetry. Likewise, the corresponding birefringence vanishes, which means that the crystal becomes isotropic. The reversible phase transition observed at t_c seems to be of the triclinic $P\bar{1} \rightarrow$ cubic $Fm3m$ symmetry, of ferroelastic–paraelastic type.

The t_c value increases with x, as well as with the enthalpy variation ΔH_{t_c} (Fig. 7). We can easily explain these results. In $(Cs,K)_3BiCl_6$ the three alkali ions are located in two positions of *CN* 6 and 12. For $x = 0$ (Cs_2KBiCl_6), a cubic symmetry is found with two large Cs^+ ions occupying the 12-coordinated sites and one smaller K^+ ion the octahedral sites. This compound remains cubic at least down to the liquid nitrogen temperature. When the number of K^+ ions exceeds *1* ($x > 0$), the presence of K^+ ions in the largest holes of the framework induces a distortion at room temperature. The materials are cubic only at higher temperatures. When x increases, the distortion becomes more important, which leads to a rising t_c and ΔH_{t_c} (Figs. 4 and 7).

This work allowed us to characterize a new family of bismuth ferroelastic materials, whose phase transition appears much higher than room temperature. This work will be given a two-way extension: correlation between structural distortions and ferroelastic properties, and elaboration of

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[1] The nonlinear optical tests were made by D. Bernard, Laboratoire de Chimie Minérale D, Université de Rennes.

$(A,B)_3BiCl_6$ single crystals of good quality and big size.

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